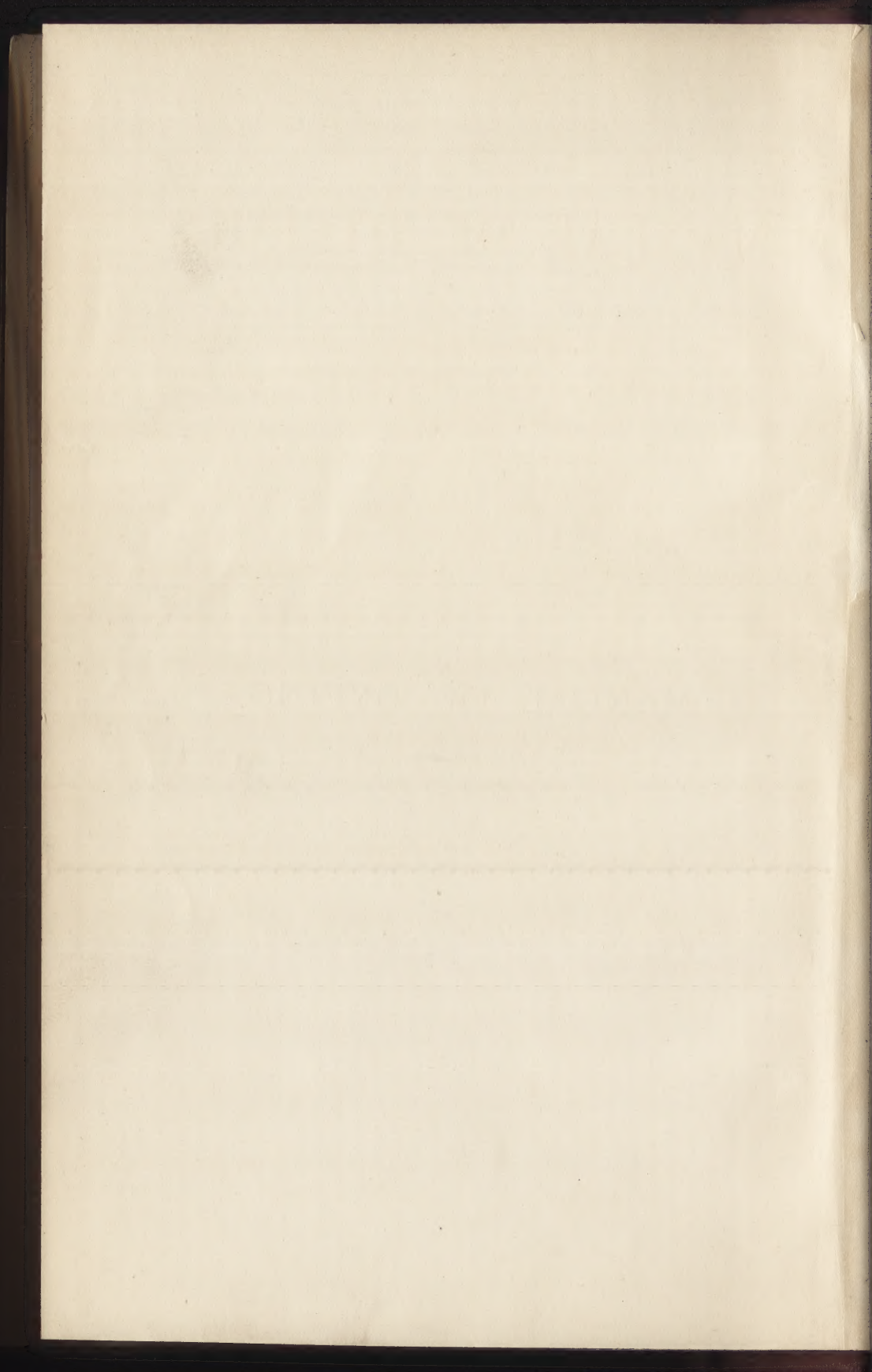


A
MANUAL OF DYEING.



A

MANUAL OF DYEING:

FOR THE USE OF PRACTICAL DYERS, MANUFACTURERS,
STUDENTS, AND ALL INTERESTED IN THE
ART OF DYEING.

BY

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WITH NUMEROUS ILLUSTRATIONS AND SPECIMENS OF DYED FABRICS.

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MANUAL OF HYGIENE

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PART VII.

ARTIFICIAL ORGANIC COLOURING MATTERS.

A NEW age was inaugurated for the art of dyeing by Perkins' discovery of mauve in 1856. Almost numberless colouring matters have since been produced from coal-tar; relatively few have stood the test of time, and most of these will probably disappear from commerce before another thirty-five years have passed; but science works indefatigably, and enriches us continuously with new and better, with more permanent and beautiful colouring matters.

The constitution of most artificial dyestuffs is well known, and scientists soon succeeded in showing the relations between their constitution and tinctorial properties.

Græbe and Liebermann, in 1868, expressed the opinion that it is chiefly an intimate connection of the atoms of oxygen and nitrogen which gives rise to the colouring character of organic compounds, and that the colouring character is destroyed if the intimate connection is loosened by the entrance of hydrogen (*leuco-compounds*). Thus,

Benzo-quinone ($\text{C}_6\text{H}_4\text{<}\overset{\text{O}}{\text{O}}\text{>}$) is yellow;

Hydroquinone ($\text{C}_6\text{H}_4\text{<}\overset{\text{O}-\text{H}}{\text{O}-\text{H}}\text{>}$) is colourless.

Azobenzene ($\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5$) is yellowish-red;

Hydrazobenzene ($\text{C}_6\text{H}_5-\text{N}-\text{N}-\text{C}_6\text{H}_5$) is colourless.



Although Græbe and Liebermann's views were pronounced almost a quarter of a century ago, when our knowledge of the chemical constitution of the dyestuffs was still very limited, they are in accordance with the modern ideas of the tinctorial character of organic compounds.

O. N. Witt published in 1876 a more comprehensive theory of the constitution of dyestuffs. According to this author a colour-bearing (chromophorous) group or *chromophor* must be introduced into the colourless aromatic hydrocarbons to render them capable of yielding a coloured substance. Benzene is colourless, but mononitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, dinitrobenzene, $\text{C}_6\text{H}_4(\text{NO}_2)_2$, and trinitrobenzene, $\text{C}_6\text{H}_3(\text{NO}_2)_3$,

are coloured and so is azobenzene, $C_6H_5N=N C_6H_5$. Those compounds which contain chromophorous groups and are coloured, but possess little colouring power, are called by Witt *chromogenes*; because they are able to generate colouring matters by taking up salt-forming groups. Thus the chromogene trinitrobenzene becomes the dyestuff trinitrophenol or picric acid, $C_6H_2(N O_2)_3(O H)$, by the entrance of the hydroxyl-group " $O H$;" azobenzene is converted into the dyestuff amidoazobenzene (fast yellow), $C_6H_5N=N C_6H_4N H_2$, by the amido-group " $N H_2$." These salt-forming groups are termed by Witt *auxochromous* groups. The dyestuffs are less coloured in the free state than in the form of salts; while the solution of picric acid is light yellow, that of sodium picrate is dark yellow; and the solution of amidoazobenzene is yellow, while that of amidoazobenzene hydrochloride is purplish. The entrance of the amido-group into the trinitrobenzene does not convert the same into a dyestuff, because its basic influence is destroyed by the acid character of the nitro-groups. The sulpho-group, $S O_3 H$, and the carboxyl-group, $C O_2 H$, although salt-forming, are not auxochromous groups, because they convert the chromogenes into weak dyestuffs only. Witt established the following principles:—

1. The tinctorial character of an aromatic substance depends on the simultaneous presence of a colour-bearing and a salt-forming group.
2. The chromophor exerts the colour-generating influence more in the salt-like compounds of the dyestuffs than in the free compounds.
3. Of two dyestuffs of analogous constitution that one is the better the salts of which are the more stable.

In various recent books the dyestuffs have been classified according to the chromophors, and this division appears the best for a scientific treatise on the colouring matters. It is, however, necessary in this case to separate substances which are closely related, in their behaviour, towards the fibres and to bring together bodies which are quite different in their general tinctorial character. We believe it to be more appropriate for a practical handbook of dyeing to divide the materials in respect to those properties which are most important to the dyer, and to describe together those dyestuffs which behave similarly in dyeing and are used in the same way and in combination with each other. Indeed, this division is not ideal and consistent in every case, since many dyestuffs are used in different ways; but it seems to us to be the most convenient for practical purposes.

We shall describe the dyestuffs in the following groups*:

I. *Direct Cotton Colours*.—Colours which dye cotton in full shades without the aid of mordants.

* Generally the dyestuffs will be described in the different groups according to the order of the colours of the rainbow. But we have not strictly followed this principle, if it seemed advisable to place similar compounds together; and in the nitro-compounds and azo-compounds of the acid colours we have begun with yellow.

II. *Basic Colours*.—Colours of a basic nature which form tannates, insoluble in water, and which dye the vegetable fibres with the aid, and the animal fibres without the aid, of mordants.

III. *Acid Colours*.—Colours of an acid nature which dye the animal fibres without the aid of mordants.

IV. The *Eosins* and *Rhodamines*.—Annex: *Corallin* and *Resorcin-blue*.

V. *Mordant Colours*.—Colours which are dyed with the aid of *metallic* mordants. (Alizarins and others.)

VI.—*Miscellaneous Colours*:—

- | | |
|--------------------|----------------------------|
| (a) Aniline-black. | (d) Insoluble azo-colours. |
| (b) Indigo. | (e) Cachou de Laval. |
| (c) Indophenol. | (f) Canarin. |

DIRECT COTTON COLOURS.

A great number of dyestuffs have been brought into commerce during the last few years which are distinguished by the common property of dyeing the vegetable fibres in full shades, and fairly fast to washing without the aid of mordants. The first of these substances was *Congo-red*, which was discovered in 1884 by Böttiger; hence the whole group, especially the derivatives of benzidine and tolidine, which are chemically related to this dyestuff, are frequently called the “Congo-colours” or “benzidine-colours.”

The direct cotton colours which are found in commerce at the present time are, without exception, sulphonates of sodium, ammonium, or potassium; but it seems that non-sulphonated bases may also possess the property of dyeing unmordanted cotton.*

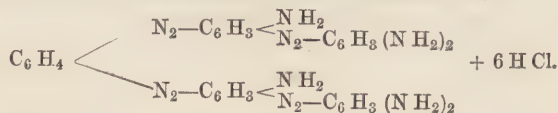
Most of the direct cotton colours are tetrazo-compounds—*i.e.*, compounds which contain the azo-group—N=N—twice in the molecule.

Azo-compounds which contain only one group—N=N—in the molecule (like the bulk of the acid colours), do not dye cotton without the aid of mordants, with the exception of certain substances like “Erika” (see below).

It would appear from this fact that the direct dyeing character of these compounds is due to the double chromophorous group.

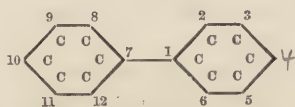
$\left\{ \begin{array}{l} \text{—N=N—} \\ \text{—N=N—} \end{array} \right.$ Not all tetrazo-colours, however, dye unmordanted cotton equally well. As a rule, only such tetrazo-compounds are direct

* Schultz and Julius, *tabell. Uebersicht*; 2nd Edition, page 56; *Catechu-brown* (Berlin) $\text{C}_{30} \text{H}_{28} \text{N}_{14} \cdot 6 \text{HCl}$ (azo-compound of one molecule of diazotised Bismarck-brown, and two molecules of metaphenylenediamine).



cotton colours, the diazo-groups of which are placed symmetrically to the connecting group. The question as to the symmetrical constitution arises chiefly in connection with the diamido-derivatives of

diphenyl $\begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_5 \end{array}$, which we may describe by the graphic formula :—



For the production of direct cotton colours those diamines derived from diphenyl have proved the most valuable, which contain the amido-groups in the positions 4 and 10—*i.e.*, *para positions to the other benzene nucleus*; and those in which the positions 2, 6, 8, and 12, *i.e.*, the *ortho positions in relation to the other benzene nucleus*, are occupied by hydrogen, not by other elements or radicals. The positions 3, 5, 9, and 11, the *meta positions in relation to the other benzene nucleus*, may be occupied by hydrogen or any other element or radical, without impairing the direct tinctorial character of the colouring matters. Those tetrazo-dyestuffs which do not readily dye unmordanted cotton act as acid colours towards the animal fibres.

It is impossible to give more than this short sketch of the constitution of the tetrazo-compounds which are capable of dyeing the vegetable fibres without the aid of mordants, since many other circumstances would have to be considered if a fuller explanation were given. This interesting subject belongs to theoretical chemistry and the limits of our space do not admit of further enlarging on it.*

Like the ordinary azo-colours, the tetrazo-colours are produced by the action of diazotised amines on phenols (naphthols) or aromatic amines or their sulphonic or carboxylic acids; thus they contain, in addition to the double *chromophorous* group N_2 , the *auxochromous* groups " N H_2 " or " O H ," or their derivatives, like " $\text{N H}(\text{C}_6\text{H}_5)$ " or " $\text{O C}_2\text{H}_5$."

The tetrazo-colours are derivatives of benzidine or tolidine (Congo-colours), diamidostilbene, azoxydiamines, and various other diamines.

In addition to the tetrazo-colours, a class of direct cotton colours is known, which are either not azo-compounds at all, or the tinctorial character of which is not due, in the first place, to their azo-group. The dyestuffs of this group are obtained from compounds, which are prepared by heating organic bases, notably paratoluidine and metaxylidine, with sulphur. In this way "thio-bases" are obtained,

the chromophorous group of which has the constitution — $\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{C}—$.

The first of these compounds is *primuline*, discovered by A. G. Green. Neither primuline nor a similar colouring matter, named *thioflavin S*,

* The subject has been recently discussed with great ability by Paul Werner in the *Moniteur Scientifique Quesneville*, 1891, pp. 22, 135, 382, 601, 830.

are azo-compounds. Several other dyestuffs—e.g., *Erika*, *cotton-yellow R*, and, in a certain sense, also *thiazol-yellow*, are azo-compounds; but undoubtedly they possess the same chromophorous group as primuline, so that the azo-group need not be considered as an essential condition for the colouring character of the compound.

The nature of the process of dyeing the vegetable fibres with these colours has not yet been explained and no chemical reaction has been discovered to take place in the dye-bath. The cotton absorbs the dyestuff by some cause, generally termed affinity (diffusion by Mueller-Jacobs; solution by O. N. Witt), and retains it with a considerable power. The colour is extracted from the fibre by water, and can be stripped to a large degree by repeated boiling out with water. Inversely, in dyeing, a part of the colouring matter is always retained by the dye-liquor, the quantity of which depends on the dissolving power of the dye-liquor and on the absorbing capacity of the fibre in regard to the dyestuff. If the former is very great—i.e., if a great quantity of water is used—a large proportion of colouring matter is retained by the dye-liquor; if the latter is considerable—i.e., if much material (compared with the amount of liquid) or, to use the common expression, if concentrated baths are used, the liquor is better exhausted. The dissolving power of the liquor can be diminished not only by decreasing the quantity of water, but also by adding soluble salts, notably common salt and Glaubersalt, also potash, soda, borax, phosphate, and stannate of soda, &c. Common salt and Glaubersalt simply diminish the dissolving power of water towards the dyestuffs (as is the case in the well-known process of “salting out”), and the other salts act probably in the same way, since most of these colouring matters are less soluble in alkaline water than in pure water. The influence of these salts, however, has not been studied except from a mere practical point of view.

On account of these circumstances cotton is dyed with the direct cotton colours in as concentrated a bath as possible, and with the addition of varying quantities of certain salts. The amount of the latter should not be so large as to precipitate the dye entirely, although it is not absolutely necessary that it be entirely in solution. A table by W. M. Gardner* is given below stating the most appropriate amounts of salts to be used. These results are based, however, on laboratory experiments, and are not quite in accordance with practical experience. It is very difficult to produce on the large scale clear and even shades with such quantities of salt as 160 grammes per litre or even half as much, and considerably smaller amounts are used in practice.

The first column states the name of the dyestuff, the second the best amount of salt to use, expressed in grammes per litre, and in the third column is found the quantity of salt which prevents dyeing;

* *Textile Manufacturer*, 1890, pp. 345, 448.

where this column is left blank, it indicates that the colour dyes even in the presence of 160 grms. of salt per litre, the highest quantity used.

I.	II.	III.	I.	II.	III.
Congo-red,	40	...	Toluylene-orange R, .	10	...
Congo-red G,	20-40	160	Mikado-orange G, . .	40-60	160
Congo-red 4 R,	40-80	160	Mikado-orange R, . .	40	160
Brilliant Congo G, . .	160	...	Heliotrope,	10-20	40
Brilliant Congo R, . .	80	...	Hessian violet, . . .	80	...
Benzopurpurin 4 B, . .	20	80	Azo-violet,	20	80
Benzopurpurin 6 B, . .	20	80	Benzo-brown G, . . .	40	...
Benzopurpurin 10 B, . .	80	160	Benzo-brown N B, . .	10-20	160
Brilliant purpurin R, .	40	160	Benzo-brown B, . . .	10-20	160
Deltapurpurin 5 B, . .	80	160	Cotton-brown N, . . .	10-20	80
Deltapurpurin 7 B, . .	20	80	Hessian brown B, . .	10-20	160
Diamine-scarlet B, . .	40	160	Hessian brown 2 B, .	10	80
Diamine-red N,	40	160	Mikado-orange 4 R, .	20-40	160
Rose-azurin B,	40	160	Chrysamin G,	20	160
Thiazol-yellow,	80	...	Chrysamin R,	10-20	160
Azo-blue,	20	80	Cresotin yellow G, . .	10	...
Benzoazurin R,	10	80	Cresotin yellow R, . .	10	100
Benzoazurin G,	20	80	Congo-yellow,	40	...
Benzoazurin 3 G, . . .	20	80	Diamine-yellow N, . .	20	...
Sulphonazurin,	10	40	Carbazol-yellow, . . .	40-80	...
Diamine-blue B,	10	40	Cotton-yellow G, . . .	40	...
Benzo-black-blue, . . .	10	20	Brilliant yellow, . . .	160	...
Congo-violet,	40-80	160	Chrysophenin,	80	160
Hessian purple N, . . .	40	160	Hessian yellow,	80	160
Hessian purple B, . . .	80	...	Curcumin S extra, . .	40	160
Hessian brilliant purple,	100	...	Curcumin W,	160	...
Congo-coriuth G,	10	40	Hessian-brown 2 M, . .	10	40
Congo-coriuth B,	10	80	Mikado-brown G, . . .	40	...
Salmon-red,	20	80	Mikado-brown M, . . .	40	...
Erika G,	20-40	80	Mikado-brown B, . . .	40-80	...
Erika B,	40	...	Alkali-brown,	20	160
St. Denis red,	special	...	Violet-black,	20	80
Benzo-orange R,	20	...	Diamine-black R O, .	10-20	80
Toluylene-orange G, . .	20-40	160			

The property of these dyestuffs to redissolve readily in water and to go on the fibre easily, prevents them from accumulating in any part of the material in unequal quantities; hence they dye the vegetable fibres very evenly, hardly any precaution being necessary to prevent unevenness. The direct cotton colours possess the property of "equalising" and "running" to such a degree that in many cases two hanks of cotton, one dyed with one of these dyestuffs and the other being white, when boiled together for a length of time in water, will acquire almost the same shade.

The nature of the process taking place in dyeing wool and silk with the direct cotton colours has not been studied; it resembles to some extent the dyeing of the "acid colours," since these dyestuffs seem to be taken up best from acid-baths by the animal fibres. On the other hand, the animal fibres may be dyed by the same methods as the vegetable fibres.

The direct cotton colours possess the property of forming lakes with the basic colours. E. Knecht* and G. Galland† have studied this reaction, which was first made known in the case of chrysamin by the Farbenfabriken vorm. Fr. Bayer & Co. They found that only the basic colours form lakes with those dyestuffs, and that the lakes are decomposed above 70° and even at lower temperatures.

Use is made of this property to produce compound shades by first dyeing with a direct colour and subsequently topping with a basic colour.

Application of the Direct Cotton Colours.—As is indicated by their general name the direct cotton colours are used for the dyeing of unmordanted cotton. In calico-printing their property of bleeding prevents them from being generally used. They are employed, however, to some extent for padding and bottoming. They find a limited employment in the dyeing of linen, jute, and the animal fibres; for linen, however, they are not fast enough, and for the other fibres a rich assortment of equally good and less expensive colours are at the disposal of the dyer. The majority of these colours are much faster to milling, when dyed on wool in an acid bath, than the ordinary acid colours, and they deserve for this reason the attention of the wool dyer. (See also below.)

Most of the direct cotton colours are dyed in neutral or alkaline baths, especially on the vegetable fibres; some, however, require slightly acid baths. They can be mixed with advantage and dyed in the same bath, to produce compound shades; those, of course, which require alkaline baths should not be mixed with such as demand acid baths. As a rule, these dyestuffs are precipitated by lime; hence calcareous water should be avoided or corrected. The best way to purify hard water for dyeing with these colours, provided an alkaline bath be required, is to add some soap and boil; a scum of lime soap will come to the surface and is easily skimmed off. All these colours are soluble in water, some indeed very sparingly, but freely enough to admit of their application in aqueous solutions.

The general mode of procedure is to prepare the bath with a solution of the whole amount of dyestuff required and with the necessary other ingredients. As little water as possible is used, and the bath should be heated with a steam coil, not with direct steam.

In the case of calcareous water the liquor is boiled with some soap, as indicated above, before the colour solution is added. The goods are entered into the fully prepared bath at a medium or high temperature and turned from time to time during 30 to 60 minutes. As a rule, the dyeing takes place at the boil, some colours, however, require a slightly lower temperature. When no more colour is taken up, the goods are removed from the bath, wrung, and then rinsed in cold water, soda solution, or Turkey-red oil (see below), and dried. The

* *Journ. Soc. Dyers and Col.*, 1886; p. 2. † *Ibid.*, 1886; p. 145.

dye-baths are not exhausted and may be used continuously; their strength is restored after each dyeing by adding as much of the ingredients as has been consumed ($\frac{2}{3}$ to $\frac{7}{8}$ of the original amount).

The direct cotton colours are stripped more or less easily from the fibres, especially from cotton and linen, by water and soap solutions; and are liable to tinge white fibres with which they come in contact in the same bath. This property of *bleeding* or *running* is very objectionable, and largely prevents their use in calico-printing and linen dyeing. In spite of this fact, however, their shades lose comparatively little in intensity on repeated soaping, and they are considered to be moderately fast, or even fairly fast to soap.

In the special description of the dyestuffs attention will not be called in each case to the property of "bleeding," as it is common to some extent to all these colours.

As a rule, the direct cotton colours are fugitive to light and certainly not faster than the basic colours. Some, however, notably chrysamin, belong to the fastest colours known. Generally they are less fugitive on the animal than on the vegetable fibres.

A great many of the direct cotton colours, especially the reds, are more or less sensitive towards the action of dilute acids, even of the acids present in the atmosphere, their shades being thereby turned blue or brownish; this defect, the cause of which is not known with certainty, may be overcome to a certain extent by charging the dyed fibre with soda or some other non-volatile alkali (see below). Some shades, particularly the yellow shades, are reddened by the action of dilute alkalies. The original shades, whether they have been changed by acids or alkalies, are easily restored by washing with water or by treatment with a very diluted counteracting chemical agent (ammonia or acetic acid respectively).

The topping of the direct cotton colours with basic dyestuffs, which has been previously mentioned, takes place in the most simple manner; the goods, after having been dyed with the direct colours, are wrung out and slightly rinsed in water (to prevent rubbing) and then worked in a tepid bath of the basic colour until the desired shade is obtained, washed, and dried. Elevated temperatures spoil the shade by decomposing the lake which is formed by the two colours. The direct colours lose in some cases the property of bleeding by this topping process, being converted into insoluble compounds.

A great number of direct cotton colours are capable of being diazotised on the fibre and forming azo-compounds with phenols, amines, &c. (primuline-ingrain colours, diamine-blacks, &c.). These new compounds, being insoluble, do not bleed either, and their formation on the fibre is a valuable method of producing shades which are fast to soap. The property of being diazotisable is common to a great number of colouring matters—*e.g.*, magenta and safranin; but little practical use has been made of it.

Recently a process has been patented by the Farbenfabriken, Elberfeld (Bayer),* to make the direct colours faster to the action of light and soap by treatment with a boiling solution of certain metallic salts. Salts of zinc, chromium, nickel, iron, and copper have been recommended for this purpose. Zinc in the form of zinc sulphate is found to be best suited for use in the dyeing of wool and silk, since, without affecting the shade, it makes the colours materially faster to washing and milling. Nickel salts make the colour redder, iron salts duller. Copper sulphate has been found valuable for certain blue and violet dyestuffs on cotton, which become greatly faster to soap on boiling in a solution of blue vitriol; azo-violet is turned less reddish and the benzoazurins more greenish by this agent. The dyestuffs which are derivatives of salicylic or cresoxylic acid and of certain sulphonic acids—*e.g.*, chrysamin, also possess the property of yielding on chromium mordants shades which are exceedingly fast to soap.

Cotton is dyed with these dyestuffs in the manner indicated above, The bath is prepared with the requisite ingredients, the colour is added at once, and the material is entered at or near the boiling point and dyed at these temperatures for 30 to 60 minutes. Most of the colours are dyed in alkaline baths, which are prepared with potash, soda, soap, borax, phosphate, silicate, aluminate or stannate of soda, to which such neutral salts as common salt or Glaubersalt are added. A number of the colours are dyed in neutral baths with only an addition of common salt or Glaubersalt. Lastly, some are dyed in a bath which is slightly acidulated with acetic or oxalic acid and contains also common salt or Glaubersalt.

In none of these cases are the baths completely exhausted, hence they should be kept for continuous use (see above).

Mercerised cotton possesses greater attraction for these colours than ordinary cotton, and assumes under similar conditions a considerably deeper shade. Fuller shades are obtained on unbleached than on bleached cotton.

The dyed goods may be dried without washing. In the case of the colours, however, which are sensitive to acids, it is of great advantage to pass the material after dyeing through a solution of soda, which may contain as much as 5 parts of soda ash in 100 parts of water. This not only protects the shade against the influence of acid gases, but it enhances the fastness to light also. Greater brilliancy is obtained by passing the dyed goods through a solution of Turkey-red oil which has been neutralised with soda.

In the case of colours which are sensitive to alkalies, the shade is sometimes brightened by weak acetic or sulphuric acid.

Linen is not dyed to any extent with the direct cotton colours, since the property of bleeding is injurious for linen goods. The same methods as for cotton are applicable for this fibre.

* *Brit. patent*, 1889; No. 3934.

The ingrain-colours, both those of primuline and of the diamine-blacks and -browns, &c., may be suitable for linen yarns, since they do not run.

Jute can be dyed in the same way as cotton, or like wool. At the present time the direct cotton colours appear rather expensive for this material.

Wool and Silk are dyed in neutral baths, or in a weak soap-bath, with or without the addition of common salt. It seems, however, to be a better method to fix all these dyestuffs on the animal fibres in a boiling bath which has been acidulated with acetic acid, and if such treatment should be required, as in the case of Congo-red, to develop the shades subsequently in a weak solution of soda. The shades are often different from those obtained on cotton, and, as a rule, faster to soap, light, and acids.

Mixed goods of Cotton and Wool or Silk are dyed in a bath not more alkaline than is required for the dyeing of the cotton fibre. About 10 per cent. of phosphate of soda or of borax, and, if necessary, 2 per cent. of potassium carbonate are added (if strong alkalinity is indispensable).

The behaviour of the direct cotton colours is not the same towards the vegetable and the animal fibres. Not only are the shades different in appearance and in fastness towards light, soap and acids; but, under the same conditions, one fibre may be dyed perfectly, while the other hardly takes up any colour. The Mikado colours furnish a striking example of this phenomenon.

A great number of the direct cotton colours resist milling exceedingly well, when dyed on wool in an acid bath, and these are applicable for yarns which are to be subjected to a moderate fulling. Diamine fast red F is of great value for this reason (see p. 419).

In the following description of the dyestuffs it has been thought expedient, on account of the great number of substances, to give their characteristic properties as briefly as possible. Their properties are given in the following order:—(1) The appearance of the dyestuff; (2) the appearance of the aqueous solution; (3) the action of hydrochloric acid on this solution, indicated by the symbol HCl ; (4) the action of strong caustic soda lye on a strong aqueous solution of the dyestuff, indicated by the symbol NaOH —the words “soluble precipitate” signify that the precipitate dissolves in pure water; (5) the colour of the solution of the dyestuff in sulphuric acid (monohydrate); and, finally, (6) the reaction which is noticed on diluting the solution with water. The other properties of the various dyestuffs will be described as far as they appear to be important in every special case.

The constitution of the azo-compounds has been briefly indicated by naming first (on the left side) the diazotised base, and then (on the right side) the other compounds on which the diazotised base acts.

CONGO-RED (Berlin, Bayer, Leonhardt, Levinstein).

Benzidine $\left\{ \begin{array}{l} \text{naphthionic acid.} \\ \text{naphthionic acid.} \end{array} \right.$

Red-brown powder; aqueous solution, orange-red; HCl , blue precipitate; NaOH , no change; solution in H_2SO_4 , blue; on diluting, blue precipitate. Congo-red is so extremely sensitive to acids that it has been recommended as an indicator for volumetric analysis.

Application.—See also general remarks (pp. 410-413). Calcareous water must be avoided or purified.

Cotton.—For a full shade boil one hour in a concentrated bath with 3 per cent. of Congo-red, 10 per cent. of sodium phosphate, and $2\frac{1}{2}$ to 5 per cent. of soap; 10 per cent. of Glaubersalt and 5 per cent. of carbonate of soda or of potash can be used instead of the phosphate. After dyeing, pass through a solution of soda (containing 2 to 5 parts of soda ash in 100 of water), wring and dry. The brilliancy is increased by passing the dyed goods through Turkey-red oil which has been neutralised with soda; if the goods are to be finished, the oil may be added to the finishing material. The following methods have also been recommended:—Boil for $1\frac{1}{2}$ hours in a bath containing the required amount of dyestuff—3 per cent. of aluminate of soda, 3 to 5 per cent. of soap, and 10 per cent. of Turkey-red oil, allow to cool in the bath, wring, and dry. Or boil for 2 hours with the necessary amount of dyestuff—3 per cent. of stannate of soda and 4 per cent. of soft soap, allow to cool in the bath over night, wring, and dry. Cotton can also be mordanted either with Turkey-red oil and alumina or with stannate of soda, and then be dyed in a second bath with Congo-red. These methods yield richer shades than the one first described.

Congo-red dyes a bright scarlet-red approaching the shade of Turkey-red, but it does not compare with this colour in fastness to washing, and it is very sensitive to air and light and to acids. Congo-red bleeds considerably in water, and the bleeding continues even after prolonged rinsing. When Congo-red dyed goods are washed with soap, the soap liquor becomes red; but the depth of the shade remains tolerably good after repeated moderate treatments, so that it may be considered moderately fast to soap. A short exposure of goods dyed with Congo-red to the air and light dulls the colour; but it will be brightened again by soaping. By continued exposure the shades are thoroughly bleached in a short time. Goods dyed with Congo-red are extremely sensitive to the action of acids, being turned blue; even the sulphurous acid contained in the air has a dulling effect. The treatment of the dyed goods with soda or soap solution, and even with neutralised Turkey-red oil, lessens the sensitiveness to acids and makes the colour a little faster to light.

Wool and Silk are dyed with Congo-red in a boiling bath containing

neutral salts, to which some soap or soda or phosphate of soda may be added. Better results are said to be obtained by dyeing at the boil in a slightly acidulated bath, and subsequently passing through a weak solution of soda. Congo-red is faster on the animal fibres than on cotton. Although wool dyed with Congo-red bleeds to some extent in a 3 per cent. soap solution, the colour may be considered to be fairly fast to milling. The shades are much faster to light and air and to acids than when dyed on cotton.

Mixed Goods are dyed with Congo-red in a boiling bath containing 10 per cent. of phosphate of soda and 2 per cent. of potassium carbonate (of the weight of the goods).

CONGO-RED G R (Berlin, Bayer, Leonhardt, Levinstein).

Benzidine $\begin{cases} \text{metanilic acid.} \\ \text{naphthionic acid.} \end{cases}$

Brown-red powder; aqueous solution, orange-red; H Cl, blue precipitate; Na O H, no change; solution in H_2SO_4 , blue; on diluting, blue precipitate.

Application and Properties.—Same as Congo-red; the shade is yellower.

CONGO-RED 4 R (Berlin, Bayer, Leonhardt, Levinstein).

Tolidine $\begin{cases} \text{naphthionic acid.} \\ \text{resorcin.} \end{cases}$

Brown-red powder; aqueous solution, orange-red; H Cl, violet precipitate; Na O H, no change; solution in H_2SO_4 , blue; on diluting, violet precipitate.

Application and Properties.—Same as Congo-red; the shade is bluer.

BRILLIANT CONGO G (Berlin, Bayer, Leonhardt, Levinstein).

Benzidine $\begin{cases} \text{betanaphthylamine disulphonic acid R.} \\ \text{betanaphthylamine monosulphonic acid Br.} \end{cases}$

Brown-red powder; aqueous solution, orange-red; H Cl, dark red-violet precipitate; Na O H, no change; solution in H_2SO_4 , blue; on diluting, violet precipitate.

Application and Properties.—Same as Congo-red; the shade is brighter and yellower. (See also next dyestuff as to application).

BRILLIANT CONGO R (Berlin, Bayer, Leonhardt, Levinstein).

Tolidine $\begin{cases} \text{betanaphthylamine disulphonic acid R.} \\ \text{betanaphthylamine monosulphonic acid Br.} \end{cases}$

Brown-red powder; aqueous solution, orange-red; H Cl, red-brown precipitate; Na O H, soluble orange precipitate; solution in H_2SO_4 , blue; on diluting, olive precipitate, turning blackish.

Application and Properties.—Same as Congo-red; the shade

resembles ordinary Congo-red, but it is more brilliant and less sensitive to acids.

Brilliant Congo G and R contain three sulpho-groups. The colours are very soluble in water, and are slowly taken up by the fibre; thus they require comparatively large quantities of salt in the bath (160 parts in 1,000 parts of liquor, *Gardner*), and a prolonged dyeing is necessary to obtain good shades.

BENZOPURPURINS (Bayer, Berlin, Leonhardt, Levinstein).

Application.—Same as Congo-red. The shades of the benzopurpurins are slightly more brilliant and slightly less sensitive to acids than that of Congo-red. The fastness to light and to washing is about the same.

BENZOPURPURIN B.

Tolidine $\left\{ \begin{array}{l} \text{betanaphthylamine monosulphonic acid Br.} \\ \text{betanaphthylamine monosulphonic acid Br.} \end{array} \right.$

Brown-red powder; aqueous solution, orange-red; H Cl, brown-red precipitate; Na O H, soluble orange precipitate; solution in H_2SO_4 , blue; on diluting, blue precipitate, which becomes brown.

Application and Properties (see above).—The shade is yellower than that of Congo-red.

BENZOPURPURIN 4 B.

Tolidine $\left\{ \begin{array}{l} \text{naphthionic acid.} \\ \text{naphthionic acid.} \end{array} \right.$

Brown-red powder; aqueous solution, orange-red; H Cl, blue precipitate; Na O H, soluble orange-red precipitate; solution in H_2SO_4 , blue; on diluting, blue precipitate.

Application and Properties (see above).—The shade is nearly the same as that of Congo-red.

BENZOPURPURIN 6 B.

Tolidine $\left\{ \begin{array}{l} \text{alphanaphthylamine sulphonic acid L.} \\ \text{alphanaphthylamine sulphonic acid L.} \end{array} \right.$

Brownish-red powder; aqueous solution, orange-red; H Cl, brown-red precipitate; Na O H, soluble orange-red precipitate; solution in H_2SO_4 , blue; on diluting, blue precipitate.

Application and Properties (see above).—The shade is bluer than those of Congo-red and benzopurpurin 4 B; it may be compared to alizarin, blue shade.

BENZOPURPURIN 10 B.

Dianisidine $\left\{ \begin{array}{l} \text{naphthionic acid.} \\ \text{naphthionic acid.} \end{array} \right.$

Brown powder; aqueous solution, scarlet-red; H Cl, blue precipitate; Na O H, soluble red precipitate; solution in H_2SO_4 , blue; on diluting, blue precipitate.

Application and Properties (see above). — Benzopurpurin 10 B dyes a crimson-red shade.

BRILLIANT PURPURIN R (Berlin, Bayer, Leonhardt, Levinstein).

Tolidine $\left\{ \begin{array}{l} \text{betanaphthylamine disulphonic acid R.} \\ \text{naphthionic acid.} \end{array} \right.$

Brownish-red powder; aqueous solution, claret-red; H Cl, black precipitate; Na OH, soluble red precipitate; solution in H_2SO_4 , violet-blue; on diluting, black precipitate.

Application and Properties.—Brilliant purpurin R shows the same properties as the benzopurpurins, and is dyed like these by the same methods as Congo-red. It is, however, somewhat faster to light than the preceding dyestuffs. It yields brilliant shades which are slightly bluer than Congo-red and benzopurpurin 4 B.

NEW RED (Geigy, Berlin, Bayer).

Diamidophenyltolyl $\left\{ \begin{array}{l} \text{naphthionic acid.} \\ \text{naphthionic acid.} \end{array} \right.$

Red powder; aqueous solution, orange-red; H Cl, blue precipitate; Na OH, soluble orange-red precipitate; solution in H_2SO_4 , blue; on diluting, blue precipitate. New red resembles benzopurpurin 4 B. By its chemical constitution it forms the connecting link between Congo-red and benzopurpurin 4 B.

Application and Properties.—Same as Congo-red. The shade is similar to that of benzopurpurin 4 B.

DELTAPURPURIN 5 B (Diamine-Red B).

Tolidine $\left\{ \begin{array}{l} \text{betanaphthylamine deltamonosulphonic acid.} \\ \text{betanaphthylamine monosulphonic acid Br.} \end{array} \right.$

Brown-red powder. Aqueous solution, orange-red; H Cl, red-brown precipitate; Na OH, soluble orange-red precipitate; solution in H_2SO_4 , blue; on diluting, brownish-yellow precipitate. Deltapurpurin 5 B resembles benzopurpurin B in general character. It may be considered as a mixture of benzopurpurin B and deltapurpurin 7 B.

Application.—Same as Congo-red. It dyes a red shade similar to that of benzopurpurin B, but less bright.

DELTAPURPURIN 7 B. (Diamine-Red 3 B). (Bayer, Berlin, Leonhardt, Levinstein).

Tolidine $\left\{ \begin{array}{l} \text{betanaphthylamine deltamonosulphonic acid.} \\ \text{betanaphthylamine deltamonosulphonic acid.} \end{array} \right.$

Brown-red powder, sparingly soluble in cold, freely in hot water; aqueous solution, scarlet-red; H Cl, brown-red precipitate; Na OH, soluble scarlet-red precipitate; solution in H_2SO_4 , blue; on diluting, brownish-yellow precipitate. The dyestuff forms a very sparingly soluble magnesium salt.

Application.—Same as Congo-red.

Deltapurpurin 7 B resembles the benzopurpurins. It dyes a shade which is similar to but not so bright as Congo-red and benzopurpurin 4 B.

DIAMINE-SCARLET B (Cassella).

Benzidine $\left\{ \begin{array}{l} \text{betanaphthol gammadisulphonic acid.} \\ \text{phenetol.} \end{array} \right.$

This dyestuff is produced by combining tetrazoditolyl with the sulphonic acid and phenol, and ethylating the azo-compound.

Red powder; aqueous solution, scarlet-red; HCl , reddish-brown precipitate; NaOH , makes the solution more yellowish; solution in H_2SO_4 , blue-violet; on diluting, reddish-brown precipitate.

Application on Cotton.—Diamine-scarlet B can be dyed in the same way as Congo-red. The following methods, however, are better adapted for this dyestuff:—Dye in a boiling bath which contains 500 grms. (5 lbs.) of Glaubersalt and 50 grms. ($\frac{1}{2}$ lb.) of oil-soap per 20 litres (20 galls.); boil $\frac{1}{2}$ to 1 hour; 25 grms. ($\frac{1}{4}$ lb.) of soda may be used in place of the soap. After dyeing rinse in water to which 2 to 4 parts of aluminium acetate (10°Tw.) have been added for every 20 parts of water. This operation increases the fastness of the colour in every respect. Or, dye in a boiling bath with the addition of 500 grms. (5 lbs.) of Glaubersalt and 100 grms. (1 lb.) of neutralised Turkey-red oil for every 20 litres (20 galls.), boiling $\frac{1}{2}$ to 1 hour; rinsing with the addition of acetate of aluminium is not required. The dye-baths may be freshened up after each operation and be used continuously. Calcareous water is to be avoided or purified.

Diamine-scarlet B dyes a bright scarlet shade which is slightly sensitive to dilute acids and not fast to light.

Wool is dyed with diamine-scarlet B in a boiling bath with the addition of sodium bisulphate.

Silk is dyed in an acidulated bath of boiled-off liquor or with the addition of tartaric acid.

DIAMINE FAST RED F (Cassella).

Benzidine $\left\{ \begin{array}{l} \text{gamma-amidonaphthol sulphonic acid} \\ \text{(combined in acid solution).} \\ \text{salicylic acid.} \end{array} \right.$

Red-brown powder; aqueous solution, claret-red; HCl , brown-red precipitate; NaOH , soluble red-brown precipitate; solution in H_2SO_4 , purplish; on diluting, brown-red precipitate.

Application.—**Cotton** is dyed as with Congo-red, either with 15 per cent. of calcined (35 per cent. of crystallised) Glaubersalt and 5 per cent. of soda ash or by the other methods.

Diamine fast red F dyes a shade of red, similar to benzopurpurin 4 B and Congo-red, but not so bright; it is not sensitive to dilute acids, and is moderately fast to light.

Wool is dyed in a neutral or slightly acid bath; the shade is fairly fast to milling and stoving, and very fast to light. Diamine fast red F resists milling exceedingly well when dyed on wool in an acid bath, and the fastness to milling becomes still better if the goods are boiled after the acid-dyeing for half an hour longer, with the addition of chromium fluoride to the old dye-bath; a quantity of chromium fluoride equal to the amount of diamine fast red F is required. The shades thus obtained rival madder-red in fastness to light and milling. This dyestuff is also to be recommended for topping vat-blues.

Silk is dyed in a bath which has been acidulated with acetic acid.

DIAMINE-RED N O (Cassella).

Ethoxybenzidine $\left\{ \begin{array}{l} \text{betanaphthylamine sulphonic acid Br.} \\ \text{betanaphthylamine monosulphonic acid F.} \end{array} \right.$

Red-brown powder; aqueous solution, scarlet-red; H Cl, black precipitate; Na O H, soluble scarlet precipitate; solution in H_2SO_4 , blue; on diluting, black precipitate.

Diamine-red N O dyes a red shade, similar to deltapurpurin 7 B (diamine-red 3 B); it shows the same sensitiveness to dilute acids as this dyestuff and the benzopurpurins, and is not fast to light.

Application.—Cotton is dyed like Congo-red; best with 10 per cent. Glaubersalt and 5 per cent. soda ash. Wool and mixed goods are dyed in neutral baths with 10 per cent. of Glaubersalt.

ROSAZURIN G (Bayer, Berlin, Leonhardt, Levinstein).

Tolidine $\left\{ \begin{array}{l} \text{methyl betanaphthylamine deltasulphonic acid.} \\ \text{betanaphthylamine deltasulphonic acid.} \end{array} \right.$

Brown-red powder; aqueous solution, cherry-red; H Cl, dark red-violet precipitate; Na O H, soluble purplish-red precipitate; solution in H_2SO_4 , sky-blue; on diluting, dark violet precipitate.

Application.—Same as Congo-red.

Rosazurin G dyes a bluish-red shade, somewhat resembling safranin; it is sensitive to dilute acids and not fast to light like most of the preceding colours.

ROSAZURIN B (Bayer, Berlin, Leonhardt, Levinstein).

Tolidine $\left\{ \begin{array}{l} \text{methyl betanaphthylamine deltasulphonic acid.} \\ \text{methyl betanaphthylamine deltasulphonic acid.} \end{array} \right.$

Red-brown powder; aqueous solution, purplish-red; H Cl, dark red-violet precipitate; Na O H, soluble purplish-red precipitate; solution in H_2SO_4 , sky-blue; on diluting, dark violet precipitate.

Application.—Same as Congo-red.

Rosazurin B strongly resembles the preceding dyestuff; it dyes a slightly bluer shade.

NAPHTHYLENE-RED (1 : 5) (B. A. S. F.)

Naphthylenediamine (1 : 5) $\left\{ \begin{array}{l} \text{naphthionic acid.} \\ \text{naphthionic acid.} \end{array} \right.$

Brown-red powder, sparingly soluble in water; aqueous solution, orange-red; HCl , black precipitate; NaOH , soluble orange-red precipitate; solution in H_2SO_4 , violet-blue; on diluting, dark blue precipitate.

Application.—Same as Congo-red. The following mode of operation helps to dissolve the colour completely in the dye-liquor:—Prepare the bath for 10 kgs. (10 lbs.) of cotton with 500 litres (50 galls.) of water, 375 grms. (6 oz.) of dyestuff, and 250 grms. (4 oz.) of soap, and bring to the boil; add 500 grms. (8 oz.) of Glaubersalt and 500 grms. (8 oz.) of carbonate of potash or any other of the alkaline salts used in dyeing these colours, enter the cotton, and boil one hour; finally treat as usual in carbonate of soda or Turkey-red oil.

Naphthylene-red yields shades similar in appearance to those of Congo-red and benzopurpurin 4 B; they are not fast to light, and are sensitive to dilute acid.

HESSIAN PURPLE N (Leonhardt, Berlin, Bayer.)

Diamidostilbene disulphonic acid $\begin{cases} \text{betanaphthylamine.} \\ \text{betanaphthylamine.} \end{cases}$

Brown-red powder; aqueous solution, cherry-red; HCl , dark blue precipitate; caustic soda, soluble crimson-red precipitate; solution in H_2SO_4 , blue; on diluting, blue-black precipitate.

Application.—The Hessian purples differ somewhat from the preceding dyestuffs.

Cotton is usually dyed with the addition of 20 per cent. of common salt only, or with 10 to 20 per cent. of salt and 5 per cent. of soda ash. After dyeing, the goods are passed through a solution of soda or Turkey-red oil.

Hessian purple N dyes a slightly bluish shade of red, which is not fast to air and light, and is slightly sensitive to dilute acids.

Wool is dyed with Hessian purple N with the addition of 10 per cent. of common salt and 5 per cent. of soda; enter luke-warm, bring to the boil and boil for half an hour. The colour is much faster on wool than on cotton, and stands milling well.

HESSIAN PURPLE B (Leonhardt, Berlin, Bayer).

Diamidostilbene $\begin{cases} \text{betanaphthylamine sulphonie acid Br.*} \\ \text{disulphonic acid} \end{cases}$ $\begin{cases} \text{betanaphthylamine sulphonie acid Br.*} \end{cases}$

Red-brown powder; aqueous solution, strawberry-red; HCl , brown-black precipitate; NaOH , soluble claret-red precipitate; solution in H_2SO_4 , blue; on diluting, dark brown precipitate.

Application.—Cotton is dyed as with Hessian purple N. The shade is a bluish-red similar to Hessian purple N.

* The betanaphthylamine sulphonie acid is not a uniform substance, but contains varying quantities of β -sulphonie acid; the difference from Hessian brilliant purple is caused by this circumstance.

HESSIAN PURPLE D. (Leonhardt, Berlin, Bayer).

Diamidostilbene $\left\{ \begin{array}{l} \text{betanaphthylamine monosulphonic acid D.} \\ \text{disulphonic acid} \quad \text{betanaphthylamine monosulphonic acid D.} \end{array} \right.$

Black powder; aqueous solution, yellowish-red; H Cl, brown precipitate; Na O H, makes the solution more bluish; solution in $\text{H}_2\text{S O}_4$, violet; on diluting, brown.

Application.—Cotton is dyed as with Hessian purple N. It is, however, preferable to dye Hessian purple D on cotton with the addition of 5 per cent. of carbonate of potash and $2\frac{1}{2}$ per cent. of soap or with the addition of 100 per cent. of common salt only, and then to pass through a solution of soda or Turkey-red oil. A bluish shade of red similar to the two preceding colours is obtained.

HESSIAN BRILLIANT PURPLE (Leonhardt, Berlin, Bayer).

Diamidostilbene $\left\{ \begin{array}{l} \text{betanaphthylamine sulphonic acid Br.} \\ \text{disulphonic acid} \quad \text{betanaphthylamine sulphonic acid Br.} \end{array} \right.$

Red-brown powder; aqueous solution, orange-red; H Cl, black precipitate; Na O H, soluble red precipitate; solution in $\text{H}_2\text{S O}_4$, violet; on diluting, blue-black precipitate.

Application.—Hessian brilliant purple is somewhat sensitive to alkalis. Cotton is dyed in a boiling neutral bath which contains a quantity of common salt equal to the weight of the material, it is then wrung out and dried without passing through a solution of soda or Turkey-red oil.

Hessian brilliant purple dyes a brighter shade than the other "Hessian purples."

CONGO-CORINTH G (Berlin, Bayer, Leonhardt, Levinstein).

Benzidine $\left\{ \begin{array}{l} \text{naphthionic acid.} \\ \text{alphanaphthol sulphonic acid N W.} \end{array} \right.$

Dark olive-green powder; aqueous solution, bluish-red; H Cl, reddish-blue precipitate; Na O H, soluble crimson precipitate; solution in $\text{H}_2\text{S O}_4$, blue; on diluting, reddish-blue precipitate.

Application and Properties.—Congo-corinth G is similar to the other benzidine colours (Congo-red and benzopurpurins, &c.). It is dyed like Congo-red, and yields maroon shades.

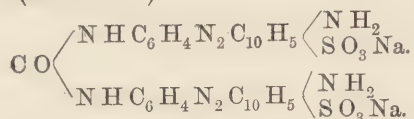
CONGO-CORINTH B (Berlin, Bayer, Leonhardt, Levinstein).

Tolidine $\left\{ \begin{array}{l} \text{naphthionic acid.} \\ \text{alphanaphthol sulphonic acid N W.} \end{array} \right.$

Greenish-black powder. Its reactions are similar to those of Congo-corinth G, which it strongly resembles in general character and tinctorial properties.

Application.—Same as Congo-red. Congo-corinth B dyes a more bluish shade of maroon than Congo-corinth G.

SALMON-RED (B. A. S. F.)



For the production of this dyestuff, para-amidoacetanilide is diazotised and combined with naphthionic acid, the acetyl group eliminated, and the product subjected to the action of phosgene gas (COCl_2).

Dark flesh-coloured powder; aqueous solution, orange-yellow; HCl , reddish-blue precipitate; NaOH , soluble orange-yellow precipitate; solution in H_2SO_4 , magenta-red; on diluting, blue precipitate.

Application.—Salmon-red is applied in the same way as Congo-red, and possesses the general character of the colours of this group. It is not fast to light, and the shade is affected by dilute acids; in fastness to washing it also resembles Congo-red, &c.

Salmon-red yields flesh-coloured to brown-orange shades.

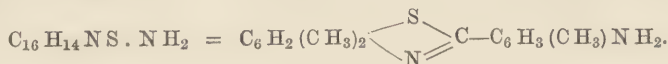
ERIKA G (Berlin, Levinstein).

Dehydrothiometaxylylidine—betanaphthol gammadisulphonic acid.

ERIKA B. (Berlin, Levinstein).

Dehydrothiometaxylylidine—alphanaphthol epsilondisulphonic acid.

These two dyestuffs are, unlike the preceding, not tetrazo-compounds, but simple azo-compounds. They are produced by the action of the diazo-compounds of dehydrothioxylylidine on naphtholsulphonic acids; dehydrothioxylylidine is a monacid base and possesses the constitution:—



It is related to dehydrothiotoluidine (see *Primuline* and *Thioflavin*).

Erika B and G show the same general reactions. Reddish-brown powder; aqueous solution, claret-red; HCl , red precipitate; NaOH , soluble crimson precipitate; solution in H_2SO_4 , red-violet; on diluting, orange-red precipitate.

Application.—Same as Congo-red.

Erika dyes pink shades which are moderately fast to light and not sensitive to a 5 per cent. solution of acetic acid; by less diluted hydrochloric acid the shade is turned yellowish. Erika shows also satisfactory fastness to washing, although it “bleeds.” Erika B dyes a bluish-pink of surpassing beauty. Erika G yields handsome yellowish-pink shades; 1 per cent. of dyestuff gives a full pink.

TITAN-PINK (Holliday).—Composition not made known.

Reddish-brown powder; aqueous solution, claret-red; HCl , red-orange precipitate; NaOH , soluble red-orange precipitate; solution in H_2SO_4 , crimson-red; on diluting, red precipitate.

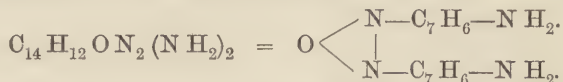
Application.—Same as Congo-red. The makers recommend dyeing in a boiling neutral bath containing $\frac{1}{2}$ kg. ($\frac{1}{2}$ lb.) of common salt per 20 litres (20 galls.) of water. A hot soaping after dyeing brightens the shade. Titan-pink yields pink shades which somewhat resemble Erika B; $\frac{1}{2}$ to 1 per cent. of colour gives a full pink.

ST. DENIS RED (Poirrier.)

Diamidoazoxytoluene $\begin{cases} \text{alphanaphthol sulphonic acid N W.} \\ \text{alphanaphthol sulphonic acid N W.} \end{cases}$

Red-brown powder; sparingly soluble in water; aqueous solution, orange-red; H Cl, red precipitate; Na OH, soluble orange-red precipitate; solution in H_2SO_4 , cherry-red; on diluting, red precipitate.

St. Denis red is different from the benzidine colours in being a tetrazo-compound of the diacid base, diamido-azoxytoluene



It is not taken up by the fibre as readily as the benzidine colours; but it yields very fine shades under suitable conditions, without the aid of mordants. In addition it possesses the property of forming lakes with metallic bases, of which fact use can be made in dyeing.

Application.—St. Denis red is dyed on cotton either with or without mordants.

Dyeing without Mordants.—For 10 kgs. (10 lbs.) of cotton dissolve 200 to 300 grms. (3 to 5 oz.) of St. Denis red in 6 litres (3 quarts) of water, in which have been dissolved 250 grms. (4 oz.) of solid caustic soda, and heat; when all is dissolved add the solution to a dye-bath prepared with 200 litres (20 galls.) of water, 48 kgs. (48 lbs.) of rock salt, and a solution of 1,750 grms. ($3\frac{1}{2}$ lbs.) of solid caustic soda in 5 litres ($\frac{1}{2}$ gall.) of water. It is essential that this bath be kept constantly at a specific gravity of $21\frac{1}{2}^\circ$ to 23° Tw. (measured at the elevated temperature of the bath). Heat the bath to 85°C ., enter the cotton, heat up to 95° , and dye during 30 minutes at this temperature; the full depth of shade is not obtained if the temperature remains below 93° , and the results are the better the nearer the bath is heated to about 98° ; *but the bath must not be brought to actual boiling.* (N.B. The boiling point of the dye-liquor is considerably above 100° , on account of the large quantity of salt it contains.) After dyeing, pass the goods without rinsing through a 1 per cent. solution of sulphuric or hydrochloric acid, rinse well in cold water, wring, and dry. St. Denis red yields by this method a brilliant Turkey-red shade, which is fast to acids, but is turned yellowish by alkalis. St. Denis red does not bleed as much as the preceding colours when simply rinsed in water; but on being rubbed with white goods it colours them; it resembles the benzidine colours in fastness to soaping, and, like these, it is not fast to light. The fastness to light is greatly

improved by passing the goods for 15 minutes from the acid bath (after a good washing) into a cold solution of 1 part of copper sulphate, or of 3 parts of common salt and 1 part of copper sulphate (*i.e.*, copper chloride) in 1000 parts of water, wringing without washing, and drying.

Dyeing with Mordants: II. Koechlin's triple mordant of aluminium, zinc, and magnesium.*—Mordant in a bath containing 1 litre (1 gall.) each of magnesium acetate (52° Tw.) and of aluminium acetate (18° Tw.) for 2 litres (2 galls.) of water; or 1.5 kgs. (1½ lbs.) of magnesium sulphate and ½ kg. (½ lb.) of alum per 10 litres (1 gall.) of water, dry, and pass for 2 minutes through an alkaline solution of zinc oxide, prepared by dissolving ½ kg. (½ lb.) of zinc sulphate and 1 kg. (1 lb.) of caustic soda solution, containing 30 per cent. NaOH in 10 litres (1 gall.) of water. Wash in water and dye in a bath containing 2 to 3 kgs. (lbs.) of St. Denis red, 400 to 500 kgs. (lbs.) of common salt, 5 kgs. (lbs.) of chalk, and 2,500 litres (250 galls.) of water; heat during 1 hour to 80°, and keep the bath at this temperature for half an hour; wash and dry.

Camille Schoen has proposed a more rapid and simple process of fixing St. Denis red—350 grms. (3½ lbs.) of St. Denis red are dissolved in 10 litres (10 galls.) of water, 200 grms. (2 lbs.) of aluminate of soda (23° Tw.), and 50 grms. (½ lb.) of a solution of caustic soda (30 per cent. NaOH). For every 10 litres (10 galls.) of this solution 1 litre (1 gall.) of a magnesia solution may be added, prepared by dissolving 400 grms. (4 lbs.) of magnesium sulphate and 200 grms. (2 lbs.) of a solution of 30 per cent. of caustic soda in 1 litre (1 gall.) of water. The pieces are made to pass through this solution, allowed to remain beamed 1 hour, then drawn through a solution containing 5 parts of alum in 100 parts, left on the roller for 2 hours, washed and dried. The goods may be passed through sodium bisulphite or ammonium chloride instead of through alum or through any bath that liberates the alumina from the aluminate, without dissolving it.

Dianthine (Br, S, and S) is very similar to, or identical with, St. Denis red.

CONGO-ORANGE R (Berlin, Bayer, Levinstein).

Tolidine $\left\{ \begin{array}{l} \text{betanaphthylamine disulphonic acid R.} \\ \text{phenol (ethylated after combination).} \end{array} \right.$

Red-orange powder; aqueous solution, red orange; HCl, brown precipitate; NaOH, soluble orange precipitate; solution in H₂SO₄, violet blue; on diluting, brown precipitate.

Application.—Congo-orange is dyed on cotton in a boiling bath with the addition of common salt only (about 10 per cent. of the weight of the cotton), or with the addition of soap, potash, &c. It is suitable for shading such direct colours as are dyed in a neutral bath—*e.g.*, Hessian purples, and benzoazurin.

* *Journ. Soc. Dyers and Col.*, 1889, p. 137.

Congo-orange R dyes a fine red-orange shade, which is similar to a very red chrome-orange. The fastness to washing is similar to that of the other benzidine colours; the fastness to light is rather better; the colour is not very sensitive to dilute acids.

Wool is dyed in a boiling bath with the addition of 5 per cent. of sodium bisulphate.

Silk and cotton and silk mixed goods are dyed with the addition of 10 per cent. of phosphate of soda in a boiling bath.

BENZO-ORANGE R (Bayer, Berlin, Levinstein).

Benzidine $\left\{ \begin{array}{l} \text{salicylic acid.} \\ \text{naphthionic acid.} \end{array} \right.$

Brown-red crystalline powder; aqueous solution, red-orange; H Cl, red-violet; Na OH, soluble orange precipitate; solution in $\text{H}_2\text{S O}_4$, violet-blue; on diluting, grey-violet precipitate.

Application and Properties.—Same as Congo-red. The shade is slightly more reddish and brilliant than that of Congo-orange and possesses about the same fastness to light, but a greater sensitiveness to dilute acids.

TOLUYLENE-ORANGE G (Oehler).

Tolidine $\left\{ \begin{array}{l} \text{orthocresol carboxylic acid.} \\ \text{metatoluylenediamine sulphonc acid.} \end{array} \right.$

Brownish-orange powder; aqueous solution, brownish-yellow; H Cl, yellowish-brown precipitate; Na OH, soluble orange precipitate; solution in $\text{H}_2\text{S O}_4$, magenta-red; on diluting, brownish precipitate.

Application—Cotton.—Boil one hour with the addition of $2\frac{1}{2}$ per cent. of oil-soap and 10 per cent. of phosphate of soda. If the water is calcareous boil the liquor with the soap before adding the dyestuff, and remove the scum of lime-soap from the surface. More reddish shades are obtained by using 5 per cent. of soda or potash instead of the phosphate. Toluylene-orange yields chrome-orange shades, from light cream to iron-buff and dark orange. The shades are moderately fast to light, soap, and dilute acids; they "bleed" in water, but not much in water containing salts, especially chalk. Toluylene-orange G is a useful padding colour for bottoming in calico-printing.

Wool is dyed with the addition of Glaubersalt and Silk in an alkaline bath or in a bath of acidified boiled-off liquor. The shade of toluylene-orange G is yellower on wool and silk than on cotton.

TOLUYLENE-ORANGE R (Oehler).

Tolidine $\left\{ \begin{array}{l} \text{metatoluylenediamine sulphonc acid.} \\ \text{metatoluylenediamine sulphonc acid.} \end{array} \right.$

Brown-red powder; aqueous solution, orange; H Cl, bluish-red

precipitate; NaOH , soluble orange precipitate; solution in H_2SO_4 , brown; on diluting, reddish precipitate.

Application and Properties.—Same as toluylene-orange G. It dyes a much redder shade of orange, which does not possess the same fastness.

MIKADO-ORANGE, G, R, 2 R, 3 R, 4 R (Leonhardt, Berlin, Bayer).

The Mikado-oranges are produced by boiling paranitrotoluene sulphonic acid with alkalis in the presence of oxidisable substances, such as glycerin, tannin, pyrogallie acid, &c. In the same way Mikado-yellow and Mikado-brown are prepared. The composition of these products has not yet been ascertained.

The general reactions of the Mikado-colours are the following:—Orange to red-brown powders; aqueous solutions, orange; HCl , reddish-brown precipitates; NaOH , soluble orange precipitates; solution in H_2SO_4 , purplish to blue; on diluting, brown precipitates.

Application.—Dye cotton in a boiling neutral bath, with the addition of 25 to 100 per cent. of common salt. Prepare the bath with the dyestuff only, enter the cotton hot, bring to the boil, gradually add the salt, boil for half an hour, rinse, and dry. The Mikado-colours can also be dyed in a bath which has been acidulated with acetic acid.

Silk and mixed goods of silk and cotton are dyed with the addition of acetic acid and common salt, soaped in a tepid bath, containing 3 parts of oil-soap in 1,000 parts, rinsed and dried.

The Mikado-oranges yield shades varying from yellow-orange to fiery-red orange, which are fairly fast to light, soap, and acids.

The Mikado-oranges show very little affinity towards the animal fibres; thus, when cotton and wool are immersed in the same bath, which has been acidulated with sulphuric acid, the shade produced on cotton is much more intense than that produced on wool.

CHRYSAMIN G (Flavophenin)—(Bayer, Berlin, Leonhardt, Levinstein).

Benzidine $\begin{cases} \text{salicylic acid.} \\ \text{salicylic acid.} \end{cases}$

Brown-yellow powder or yellow paste, sparingly soluble in water; aqueous solution, brownish-yellow; HCl , brown-yellow precipitate; NaOH , soluble orange-red precipitate; solution in H_2SO_4 , violet-red; on diluting, brown precipitate.

Application.—In dyeing with chrysamin calcareous water must be avoided or purified by boiling with soap and removing the scum of lime-soap, before the solution of the dyestuff is added. Chrysamin is extremely sensitive towards copper salts, being turned thereby into a brownish-orange; hence it must not be brought into contact with copper, and no copper vessel should be used in dyeing. Chrysamin forms lakes with chromium, and can be dyed on the vegetable and

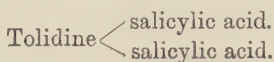
animal fibres with the aid of this mordant. The shades are very fast to soap and light.

Cotton.—Chrysamin is dyed on cotton in a boiling bath with the addition of 10 per cent. of phosphate of soda and $2\frac{1}{2}$ per cent. of soap. A pure reddish-yellow shade is obtained which is very fast to light, to washing, and to dilute acids; alkalies turn the shade into red; but the original colour is restored by washing. Chrysamin is especially well adapted to serve as a mordant for basic colours, and countless compound shades can be produced by dyeing goods first in chrysamin and topping them with magenta, malachite-green, methylene-blue, methyl-violet, &c.; the topping may take place in a cold bath and must not be done at a high temperature, since the lake is destroyed and the shade becomes dirty at about 70° . Chrysamin is also used with advantage for shading alizarin-reds and for dyeing printed goods in light tints, so as to colour the white spots yellowish and to shade the printed colours.

Wool.—Chrysamin is not very valuable as a wool-dye; wool may be dyed by the same methods as cotton.

Silk is also dyed with chrysamin like cotton.

CHRYSAMIN R (Bayer, Berlin, Leonhardt, Levinstein).



Brown-yellow powder, slightly more soluble in water than chrysamin G; aqueous solution, dark reddish-orange; HCl, brown-yellow precipitate; NaOH, soluble orange-red precipitate; solution in H_2SO_4 , red violet; on diluting, brownish precipitate.

Application and Properties.—Same as chrysamin G. The shade is more reddish.

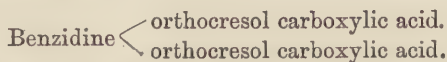
NEW YELLOW (Geigy, Berlin, Bayer).



Dark greyish-brown powder; aqueous solution, yellow; HCl, dark precipitate; NaOH, soluble brownish-orange precipitate; solution in H_2SO_4 , crimson; on diluting, yellow-brown precipitate. New yellow forms by its chemical constitution the connecting link between chrysamin G and R analogously to new red in relation to Congo-red and benzopurpurin 4 B.

Application and Properties.—Same as chrysamin G. The shade is a more reddish-yellow.

CRESOTIN-YELLOW G (Oehler).

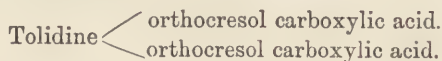


Orange-brown powder, sparingly soluble in water; aqueous solution,

brownish-yellow; HCl , olive-brown precipitate; NaOH , soluble brownish-orange precipitate; solution in H_2SO_4 , crimson; on diluting, blackish-brown precipitate.

Application and Properties.—Same as chrysamin G. The shade is similar to that of chrysamin G.

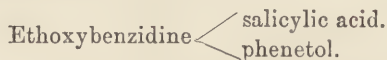
CRESOTIN-YELLOW R (Oehler).



Orange-brown powder, more soluble in water than cresotin-yellow G; aqueous solution, yellow-brown; HCl , dark brown precipitate; NaOH , soluble red-orange precipitate; solution in H_2SO_4 , violet; on diluting, black-green precipitate.

Application and Properties.—Same as chrysamin G. The shade is similar to that of chrysamin R.

DIAMINE-YELLOW N (Cassella).



This dyestuff is produced by combining diazotised ethoxybenzidine with salicylic acid and phenol, and subsequently ethylating the tetrazo-compound.

Soluble yellow paste, very sparingly soluble in water; aqueous solution (on addition of ammonia), yellow; HCl , dark greenish-yellow precipitate; NaOH , reddish-yellow precipitate; solution in H_2SO_4 , violet; on diluting, dark greenish-yellow precipitate.

Application and Properties.—Same as chrysamin G (also as to fastness). The shade is similar to that of chrysamin R.

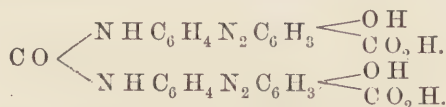
CARBAZOL-YELLOW (B. A. S. F.)



Yellow-brown powder; aqueous solution, dark orange; HCl , dark brown precipitate; NaOH , dark orange colour; solution in H_2SO_4 , blue; on diluting, brownish-black precipitate.

Application same as chrysamin G. Carbazol-yellow yields golden-yellow shades, which are fairly fast to light and soap, but sensitive to dilute acids and alkalis. It yields on chromed wool shades which are similar to fustic; they are less fast to light than fustic, but very fast to soap.

COTTON-YELLOW G (B. A. S. F.)



This dyestuff is produced analogously to salmon-red by combining

diazotised para-amidoacetanilide with salicylic acid, eliminating the acetyl group and subjecting the product to the action of phosgene gas.

Light-yellow powder; aqueous solution, dirty yellow; H Cl, dark brown precipitate; Na O H, soluble orange-yellow precipitate; solution in H_2SO_4 , orange-yellow; on diluting, at first violet, then dark brown precipitate.

Application and Properties.—Same as chrysamin G. The shade is canary-yellow, and is changed by dilute acids. Cotton-yellow G can also be fixed on chromium mordant, when it will be very fast to boiling soap solution.

BRILLIANT YELLOW (Leonhardt, Berlin, Bayer).

Diamidostilbene disulphonic acid $\begin{matrix} \text{phenol.} \\ \text{phenol.} \end{matrix}$

Light brown (terra-cotta) powder; aqueous solution, reddish-yellow; H Cl, dark blue precipitate; Na O H, red-orange colour; solution in H_2SO_4 , crimson; on diluting, blue precipitate.

Application.—Brilliant yellow is dyed in an acid bath, which is prepared with $2\frac{1}{2}$ per cent. of acetic acid and 10 to 50 per cent. of common salt. Good results are obtained by dyeing at 70°C .

Brilliant yellow yields a golden-yellow shade, which is very fast to light and dilute acids, but very sensitive to alkalis, which redden it; the shade loses considerably on soaping.

CHRYSOPHENIN (Leonhardt, Berlin, Bayer).

Diamidostilbene disulphonic acid $\begin{matrix} \text{phenetol.} \\ \text{phenetol.} \end{matrix}$

Chrysophenin is produced by ethylating brilliant yellow.

Orange-yellow powder, sparingly soluble in cold water, freely in hot water; aqueous solution, yellow; the hot solution separates the dyestuff on cooling in form of a flocculent precipitate; H Cl, violet-black precipitate; Na O H, yellow precipitate; solution in H_2SO_4 , crimson; on diluting, dark blue precipitate.

Application.—Chrysophenin is dyed on cotton in a boiling neutral bath with the addition of 10 to 50 per cent. of common salt. It can also be dyed by the method indicated for chrysamin G, or with common salt and soap, &c.

Wool may be dyed very fast to milling in an alkaline or acid bath. In the latter case the bath is prepared with the required amount of dyestuff and 2 per cent. of sulphuric acid; the wool is entered into the bath, and it is heated to the boil.

Chrysophenin is very fast to soap, light and dilute acids both on cotton and on wool; it is especially valuable on account of its being little sensitive to alkalis. It dyes a fine yellow shade similar to chrysamin R, less reddish than brilliant yellow.

HESSIAN YELLOW (Leonhardt, Berlin, Bayer).

Diamidostilbene disulphonic acid $\begin{cases} \text{salicylic acid.} \\ \text{salicylic acid.} \end{cases}$

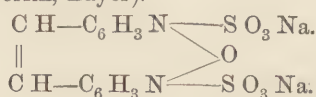
Ochre-yellow powder; aqueous solution, brownish-yellow; H Cl, brown-black precipitate; Na OH, red solution; solution in $\text{H}_2\text{S O}_4$, crimson; on diluting, dirty blue precipitate.

Application.—Hessian yellow is dyed on cotton in a boiling bath with the addition of 10 to 50 per cent. of common salt and $2\frac{1}{2}$ per cent. of acetic acid. It may also be dyed in a neutral bath. It is very fast to light and dilute acids, but not fast to soap, and rather sensitive to alkalies. The shade is slightly redder than that of brilliant yellow.

Hessian yellow is very sensitive towards the action of copper salts, and must not come into contact with copper.

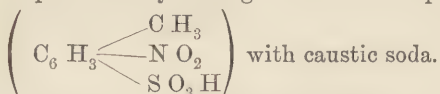
CURCUMIN S (Leonhardt, Berlin, Bayer).

(*Sun yellow, Mais*)



(Curcumin W is the corresponding ammonium salt.)

Curcumin S, the sodium salt of *azoxy stilbene disulphonic acid*, is produced by boiling a solution of paranitrotoluene sulphonic acid



Curcumin S forms a reddish-brown powder; aqueous solution, brownish-yellow; H Cl, brown precipitate; Na OH, soluble orange precipitate; solution in $\text{H}_2\text{S O}_4$, violet; on diluting, orange precipitate. Curcumin W is similar.

Application.—Curcumin is dyed in a boiling bath with the addition of 10 to 50 per cent. of common salt and $2\frac{1}{2}$ per cent. of acetic acid. It may also be dyed in a neutral bath. These processes are applicable for both vegetable and animal fibres. Silk may also be dyed in acidulated boiled-off liquor. For union goods a bath containing 100 per cent. of common salt and 5 per cent. of bisulphate of soda gives good results.

Curcumin yields a reddish-yellow, in full shades an orange colour, which resists even comparatively strong acids, but is turned red by alkalies. It is inferior to chrysamin, chrysophenin and brilliant yellow in fastness to light and soap.

MIKADO-YELLOW (Leonhardt, Berlin, Bayer).

This dyestuff is prepared in the same way as the Mikado-oranges, and possesses the same reactions and general properties as these compounds; its composition is also not yet known.

Application and fastness to light, soap, &c., same as the Mikado-oranges. Mikado-yellow dyes wool better than the Mikado-oranges.

THIAZOL-YELLOW (Bayer). **CLAYTON-YELLOW** (Clayton).

Diazoamidocompound produced by the action of the diazotised dehydrothiotoluidine sulphonic acid on dehydrothiotoluidine sulphonic acid.

Brownish-yellow powder; aqueous solution, dark yellow; HCl, orange precipitate; NaOH, soluble red-orange precipitate; solution in H_2SO_4 , yellow; on diluting, yellow precipitate (on addition of much water only).

Application.—**Cotton** is dyed as with chrysamin G or with the addition of 5 per cent. of phosphate of soda, 5 per cent. of common salt, and 2 per cent. of soap, &c.

Silk may be dyed with the addition of soap and sodium phosphate. Thiazol-yellow or Clayton-yellow is very fast to soap, and moderately fast to light; it is slightly reddened by alkalies, more so by dilute acids.

THIOFLAVIN S (Cassella), $\text{C}_{16}\text{H}_{15}\text{N}_2\text{S} \cdot \text{SO}_3\text{Na}$, is the sodium salt of *dimethyl dehydrothiotoluidine monosulphonic acid* (see *Thioflavin T*, p. 471).

Orange-yellow powder; aqueous solution, golden-yellow; HCl, brownish-yellow precipitate; NaOH, soluble yellow precipitate; solution in H_2SO_4 , light brownish-yellow with a blue fluorescence; on diluting, orange-yellow precipitate; the alcoholic solution is yellow with a green fluorescence.

Application.—**Cotton** and **satin** are dyed with the addition of 5 per cent. of oil-soap, **wool** with the addition of 10 per cent. of sodium sulphate in a boiling bath.

Thioflavin S is not fast to light; it is not sensitive to alkalies, but is turned red by dilute acids.

PRIMULINE (Br., S., & S). **THIOCHROMOGEN** (Dahl). *Carnotin, Polychromin, Aureolin, Sulphin.*

This dyestuff, which is brought into the market under a great variety of names by a number of firms, was discovered by Arthur G. Green,* chemist to Messrs. Brooke, Simpson & Spiller. Primuline is the sodium sulphonate of the *primuline-base* which is produced by heating paratoluidine with sulphur to a high temperature. The composition of the primuline-base is probably $\text{C}_{23}\text{H}_{18}\text{N}_4\text{S}_3$,† and the product seems to be formed by the condensation of 4 molecules of paratoluidine and 3 atoms of sulphur; it probably contains the chromophorous group $\begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} \text{C}$ —three times. According to a German patent of Dahl & Co., which firm discovered the reaction of sulphur on paratoluidine, the primuline-base is a mixture of bases; and *thiochromogen* would appear to be a purified and uniform substance in

* *Journ. Soc. Dyers and Col.*, 1888, p. 39.

† A. G. Green, *Journ. Soc. Dyers and Col.*, 1889, p. 81.

contrast with ordinary primuline ; greater fastness and tinctorial power is claimed for thiochromogen.

Primuline-base is a bright yellow powder which is nearly insoluble in all solvents. The alcoholic solution shows a green-yellow fluorescence. It is an extremely stable compound, not being decomposed when heated to 400° C. The salts are insoluble in water and dissociated thereby.

The dyestuff—i.e., the sodium salt of sulphonated primuline-base—forms a yellow powder, which is very soluble in hot water, but little soluble in alkaline water ; aqueous solution, yellow (if very diluted it shows a blue fluorescence) ; H Cl, dark yellow precipitate ; Na OH, sparingly soluble, light yellow precipitate ; solution in H₂SO₄, pale yellow, with a blue fluorescence ; on diluting, orange-yellow precipitate.

In contrast to the benzidine colours, primuline is not decolorised by reducing agents (not being an azo-compound) ; it cannot be discharged, nor can it be stripped by any practical means. By oxidising agents, such as chromic acid and chloride of lime, it is attacked, but not destroyed. Primuline contains an amido-group ; it can, therefore, be diazotised and combined with naphthol, &c., to form azo-compounds of yellow, red, blue, and other shades. Use is made of this fact to produce the so-called "*ingrain colours*" on the fibre (see below). The diazo-compound of primuline is decomposed by the active rays of light and by heat, thus losing the property of forming azo-compounds. Primuline forms lakes with the basic colours, and can serve as a mordant for them like the preceding dyestuffs.

Thiazol-yellow and thioflavin S are chemically related to primuline, being also derivatives of compounds produced by the action of sulphur on paratoluidine at high temperatures, and possessing the chromophorous group, $\begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix}$ C. Thioflavin S, like primuline, cannot be reduced or stripped from the fibre.

Application.—Cotton is dyed with primuline as with the preceding colours in a boiling neutral or alkaline bath ; the best addition is common salt ; Glaubersalt, soda, &c., may be used.

Wool and silk can be dyed in a neutral, acid, or alkaline bath, preferably in a bath slightly acidulated with acetic acid ; if dyed from a neutral or alkaline bath, salt must be added.

In dyeing **mixed goods** good results are obtained from an alkaline bath with the addition of salt. The affinity of the colour for the vegetable and animal fibres can be controlled by regulating the alkalinity and temperature of the bath ; the addition of soda or lowering of the temperature tend to diminish the affinity of primuline for the wool, whilst a slight addition of acid or raising of the temperature has the contrary effect.

Primuline dyes a greenish-yellow shade, similar to that of the primrose (*Primula*), which is very fast to soap and entirely unaffected by alkalis, but not fast to light. Acetic acid has no action on the shade,

mineral acids redden it. Chromic acid changes the shade to olive, whilst an alkaline solution of bleaching-powder or sodium hypochlorite converts it on boiling into an orange-yellow, which is very fast to all agents.

INGRAIN COLOURS OF PRIMULINE.

The diazotisation of primuline and combination with phenols and amines, to produce azo-colours, can be readily performed on the fibre, as discovered by A. G. Green, the inventor of primuline.* In this way a great variety of shades can be obtained which are characterised by great fastness to soaping, milling, acids, &c. Their fastness in this respect is far greater than that of the ordinary direct cotton colours, in spite of the fact that the ingrain colours are soluble in caustic soda, when prepared away from the fibre.

The phenols and amines employed are sold in solution ready for use as the so-called "developers" (Br, S, and S) or dye-salts (Dahl)—*e.g.*, as "yellow developer," "red developer," "brown developer," &c. Phenol gives yellow; resorcin, orange; betanaphthol, red, and alphanaphthol, maroon colours; metaphenylene diamine and alphanaphthylamine produce browns; and amidoazobenzene a purple shade. The sulphonic acids of betanaphthol, like Schäffer's acid or "R salt," are also used for the production of scarlet to bluish-red colours.

The method of procedure for dyeing a full ingrain colour is as follows:—The cotton is dyed in a strong boiling bath containing about 5 per cent. of primuline and, in addition, common salt; the bath is used continuously, being freshened up with 2 to 3 per cent. of primuline, &c. After having been dyed with the primuline, the cotton is thoroughly washed in cold water, to remove surface colour, and is then passed through the diazotising bath, which contains 1 part of sodium nitrite in 200 parts of cold water and sufficient sulphuric acid to taste distinctly sour (about twice the amount of the nitrite). The formation of the diazo-compound is complete in less than a minute, the colour changing to orange. After washing, the cotton is ready to be developed to the required colour. This development should be proceeded with without unnecessary delay, for, like all diazo-compounds, the diazotised primuline is unstable and begins to decompose within an hour or two, or even immediately when exposed to the light. Thus a very short exposure is liable to produce considerable unevenness, so as to spoil the goods.

The nitrite bath also can be used continuously; if it does not smell of nitrous acid or is not sufficiently acid, nitrite or sulphuric acid respectively is added; a moderate excess of either substance is not injurious.

If, for instance, it is required to produce *ingrain-red*, the diazotised cotton, after being washed, is passed at once into a bath containing in 20 to 40 parts one part of the red developer. The colour is formed at once and the development is complete in 2 or 3 minutes, except in the

* *Journ. Soc. Dyers and Col.*, 1888, p. 40.

case of very impervious material. The developing bath may be cold, warm, or even boiling; soap may be added if desired; impervious materials are best developed boiling.

The *ingrain-red* possesses great fastness to soaping and milling, acids and alkalies; but it is not very fast to light.

The development bath can also be used continuously, if fresh developer is added as it becomes exhausted. If the diazotisation or the development be incomplete—on account of the baths being too weak or not in the right condition—the colours produced are extremely fugitive to light. The yellow, orange, red, and maroon developers are alkaline solutions of various phenols, and in order to develop properly the developing bath must remain alkaline; this may be done by the addition of ammonia, soda, or, better, with acetate of soda or borax. On the other hand, the purple and brown developers, being salts of amidoazo-compounds, are acid and develop in acid solutions; if properly handled there will be no occasion to correct their acidity.

Some of the ingrain colours, especially the red and orange, are very sensitive to copper salts, small traces of these having a dulling effect on them; hence no copper vessels or pipes should be used.

All the other ingrain colours are produced by the same process as has been described for the red, except that in the last operation the corresponding “developers” are employed. The depth of shade obtained will, of course, depend chiefly upon the depth of the original primuline shade.

Ingrain-maroon produces pink to bluish-red; *ingrain-brown*, No. 1, is a terra-cotta; *ingrain-brown*, No. 2, a chocolate-brown. *Ingrain-yellow* is an orange-yellow shade, which is faster to light than the rest. *Ingrain-orange* resembles chrome-orange, and *ingrain-purple* gives reddish-indigo shades. The latter are changed to brown by alkalies; acids restore the original purple shades.

On the whole the character of the ingrain shades is the same as that of ingrain-red in point of fastness to light, soap, milling, acids, &c.

The brown and purple developers being solutions of amines, the ingrain-browns and -purples are amidoazo-compounds, capable of rediazotisation, and give a variety of dark shades, when re-combined with amines and phenols (for instance, in the form of the ordinary developers).

Developers of the alkaline class, of course, cannot be mixed with those of the acid kind to produce compound shades. Moreover, the developers of the same class can only be mixed to a limited extent, for their rate of development varies considerably.

The ingrain colours possess also the property of forming lakes with the basic colours and serve as mordants for them.

Linen.—The ingrain colours, being fast to washing, are of some value for the dyeing of linen. The method of procedure is exactly the same as on cotton.

A number of the ingrain colours are prepared away from the fibre and used as direct cotton colours—*e.g.*, alkali-yellow. (See below).

According to a patent of Ch. Dreifuss (Eng. Pat. 1888, No. 9280), the insoluble azo-colours prepared from diazotised primuline with phenols—*e.g.*, with betanaphthol, ingrain-red—can be made soluble by heating with sodium bisulphite. The products are decomposed by alkali and by steaming, and can be used as steam colours in printing.

ALKALI-YELLOW (Dahl) or **COTTON-YELLOW R** (B.A.S.F.), or **ORIOLE** (Geigy).

Under these different names an azo-dyestuff is sold which is prepared by the action of one equivalent of diazotised primuline on one equivalent of salicylic acid. It can be produced on the fibre in the form of an ingrain colour.

Brownish-yellow powder; aqueous solution, orange-yellow; HCl , yellow precipitate; NaOH , soluble orange precipitate; solution in H_2SO_4 , red-orange; on diluting, yellow precipitate. This dyestuff forms insoluble lakes with chromium oxide, like many other derivatives of salicylic acid; use is made of this property in calico-printing.

Application.—Same as Chrysamin G. The shade is a reddish-yellow. Alkali yellow is fairly fast to soap, but not to light; it is not affected by dilute acids, but is reddened by alkalies.

MIMOSA (Geigy).

This is the product of the reaction of ammonia on diazotised primuline. The constitution of this body is not known.

Cinnamon-brown powder; aqueous solution, yellow; HCl , orange precipitate; NaOH , orange; solution in H_2SO_4 , yellow; on diluting, orange precipitate.

Application.—Mimosa is applied, like primuline, in a boiling neutral bath with the addition of common salt. The shade is fairly fast to soap, but not fast to light; it is reddened by dilute acids and turned to a brownish-orange by alkalies.

AZO-BLUE (Bayer, Berlin, Leonhardt, Levinstein).

Tolidine $\left\{ \begin{array}{l} \text{alphanaphthol sulphonic acid N W.} \\ \text{alphanaphthol sulphonic acid N W.} \end{array} \right.$

Black powder with a metallic lustre; aqueous solution, violet; HCl , violet-blue precipitate; NaOH , soluble dark-red precipitate; solution in H_2SO_4 , blue; on diluting, violet-blue precipitate.

Application.—Same as Congo-red.

If the temperature is kept below 80° a less reddish shade is obtained than at the boil. Treatment with copper sulphate (see *Benzoazurin G*, p. 436) makes the colour faster to light and more greenish-blue.

Azo-blue dyes a dull reddish shade of blue, which possesses the general character of the benzidine colours, being fairly fast to washing, but not fast to light. It is not sensitive to dilute acids or alkalies.

BENZOAZURIN G (Bayer, Berlin, Leonhardt, Levinstein).

Dianisidine $\left\{ \begin{array}{l} \text{alphanaphthol monosulphonic acid N W.} \\ \text{alphanaphthol monosulphonic acid N W.} \end{array} \right.$

Black powder with a bronze lustre; aqueous solution, blue-violet; H Cl, blue-violet precipitate; Na O H, crimson colour; solution in $\text{H}_2\text{S O}_4$, blue; on diluting, blue-violet precipitate.

Application.—Same as Congo-red. After the dyeing, wash, and then work the cotton for 30 minutes in a boiling bath, containing 5 per cent. (of the weight of the material) of copper sulphate; wash and dry. Calcareous water should be avoided or purified by boiling with soap.

Benzoazurin G dyes a reddish indigo-blue shade which is fairly fast to soap, and moderately fast to light; it bleeds like the benzidine colours, but it is not affected by dilute acids or alkalies. The treatment with blue vitriol is not absolutely necessary; it makes the shade less reddish and essentially faster to light and soap.

Benzoazurin R is a mixture of benzoazurin G and azo-violet. It dyes a redder shade of blue than benzoazurin G.

BENZOAZURIN 3 G (Bayer, Berlin, Leonhardt, Levinstein).

Dianisidine $\left\{ \begin{array}{l} \text{alphanaphthol sulphonic acid Cl.} \\ \text{alphanaphthol sulphonic acid Cl.} \end{array} \right.$

Greyish-black powder; aqueous solution, blue-violet; H Cl, blue-violet precipitate; Na O H, violet-red colour; solution in $\text{H}_2\text{S O}_4$, blue; on diluting, blue-violet precipitate.

Application and Properties.—Same as Benzoazurin G. The shade is less reddish, and becomes on treatment with blue vitriol still more greenish.

BRILLIANT AZURIN 5 G (Bayer, Berlin, Leonhardt, Levinstein).

Dianisidine $\left\{ \begin{array}{l} \text{dioxynaphthalene alphasulphonic acid.} \\ \text{dioxynaphthalene alphasulphonic acid.} \end{array} \right.$
(from alphanaphthol disulphonic acid Sch.)

Greyish-black powder; aqueous solution, blue-violet; H Cl, blue precipitate; Na O H, red colour; solution in $\text{H}_2\text{S O}_4$, green-blue; on diluting, dark reddish-blue precipitate.

Application—Cotton.—Boil one hour with the addition of 50 per cent. of Glaubersalt and 5 per cent. of phosphate of soda, rinse well and dry; it is advisable to acidulate the rinsing bath with acetic or sulphuric acid. After the dyeing, the material may be worked for half an hour in a boiling solution of copper sulphate (5 per cent. of the weight of the cotton).

Calcareous water should be avoided in dyeing or purified with soap. No more soap, however, should be added than is required to remove the lime from the water. Brilliant azurin is very incompletely taken up from a bath containing soap, potash, or soda, and these materials

should not be used in dyeing with brilliant azurin either alone or in combination with other colours.

Brilliant azurin 5 G dyes a very pure and brilliant greenish shade of blue, which is fairly fast to soap and moderately fast to light. It is not affected by dilute acids or alkalis. The treatment with copper sulphate increases the fastness in every respect and makes the shade more greenish.

Wool.—Brilliant azurin 5 G is dyed on wool in a boiling bath, with the addition of 1 per cent. of sulphuric acid and 10 per cent. of Glaubersalt, and yields a fine marine-blue; it can be shaded with all acid colours. On treatment with a boiling solution of copper sulphate fairly fast shades of vat-indigo-blue are obtained.

Silk is dyed like wool or in an acidulated bath of boiled-off liquor.

Mixed goods of cotton, with wool or silk, are dyed like cotton goods.

SULPHONAZURIN (Bayer, Berlin, Leonhardt, Levinstein).

Benzidine sulphon disulphonic acid $\left\{ \begin{array}{l} \text{phenyl betanaphthylamine.} \\ \text{phenyl betanaphthylamine.} \end{array} \right.$

Dark blue powder; aqueous solution, greenish-blue; H Cl, dark blue precipitate; Na O H, blue precipitate, soluble in water; solution in $\text{H}_2\text{S O}_4$, violet; on diluting, black-violet precipitate.

Application.—Sulphonazurin can be dyed on cotton exactly like Congo-red and the other benzidine colours; the best method is to dye one hour in a boiling bath, with the addition of 10 per cent. of Glaubersalt and 10 per cent. of acetate of sodium. It is fairly fast to washing, acids, and alkalis, but not fast to light.

DIAMINE-BLUE 3 R (Cassella).

Ethoxybenzidine $\left\{ \begin{array}{l} \text{alphanaphthol sulphonic acid N W.} \\ \text{alphanaphthol sulphonic acid N W.} \end{array} \right.$

Dark powder with a bronze lustre; aqueous solution, violet; H Cl, red-violet precipitate; Na O H, crimson colour; solution in $\text{H}_2\text{S O}_4$, blue; on diluting, violet precipitate.

Application.—**Cotton** is dyed in a boiling bath, containing 15 per cent. of sodium sulphate and 5 per cent. of soda ash. **Wool** is dyed with the addition of Glaubersalt only. **Silk** and **satins** are dyed with the addition of 10 per cent. of phosphate of soda. Diamine-blue 3 R dyes a reddish shade of blue, fairly fast to washing and to light. The shade is not altered by dilute acids or alkalis.

DIAMINE-BLUE B (Cassella).

Ethoxybenzidine $\left\{ \begin{array}{l} \text{betanaphthol deltadisulphonic acid.} \\ \text{alphanaphthol sulphonic acid N W.} \end{array} \right.$

Brown-black powder with a bronze reflex; aqueous solution, blue-violet; H Cl, blue precipitate; Na O H, violet colour; solution in $\text{H}_2\text{S O}_4$, blue; on diluting, blue precipitate.

Application and Properties.—Same as diamine-blue 3 R. The shade is a pure blue. It becomes faster to light by treatment with a boiling solution of copper sulphate.

The manufacturers of diamine-blue have recently introduced improved makes of blue under the names of **Diamine-blue B X, 2 B, and 3 B.** *Diamine-blue B X* is similar to diamine-blue B; greater fastness to light and soap is claimed for this article. *Diamine-blue 2 B* and *3 B* are greener, brighter, and purer in shade than diamine blue B and B X.

Cotton is dyed with diamine-blue B X, with the addition of 15 per cent. of calcined Glaubersalt and 5 per cent. of soda crystals; for diamine-blue 2 B and 3 B double the quantity of Glaubersalt or 30 per cent. of common salt and 5 per cent. of soda crystals are required.

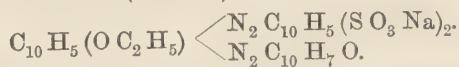
Wool is dyed with the addition of 10 per cent. of sodium bisulphate; chromed wool yields shades which are somewhat brighter, and resist milling slightly better.

Silk is dyed in a soap bath, with the addition of sulphuric or acetic acid. In an alkaline bath the silk takes up but little colour.

Satins.—When dyed with the addition of 5 per cent. of soda or 10 per cent. of soap and 20 per cent. of common salt, the cotton will acquire a bright blue, leaving the silk nearly white.

These blues can be diazotised on the fibre and combined with developers—*e.g.*, alpha- or betanaphthol or phenylene diamine; they yield in this way shades from grey to black, which are very fast to soap.

DIAMINE-BLUE 6 G (Cassella).

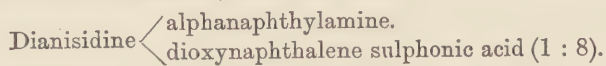


This dyestuff is prepared by combining diazotised betanaphthylamine gamma disulphonic acid with amidonaphthol ether (1 : 2), re-diazotising and combining with betanaphthol.

Dark violet powder; aqueous solution, dark blue; H Cl, violet precipitate; Na OH, makes the solution slightly duller; solution in H₂SO₄, bluish-green; on diluting, violet precipitate.

Application.—Same as diamine blue 3 R. The shade is a pure greenish-blue, which is fast to dilute acids and alkalies, but not fast to light. Wool and silk may be dyed in acid baths.

BENZO-INDIGO-BLUE (Bayer, Levinstein).

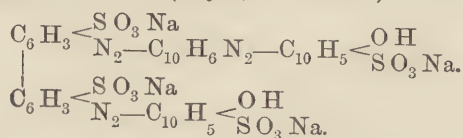


Grey powder; aqueous solution, dull blue; H Cl, blue precipitate; NaOH, reddish-blue precipitate, soluble in water; solution in H₂SO₄, dark greenish-blue; on diluting, blue precipitate.

Application.—**Cotton** is dyed in a boiling bath for 1 hour with

the addition of 2 per cent. of soap and 5 per cent. of potash or soda. After dyeing, it is rinsed in cold water, to which some acetic or sulphuric acid may be added with advantage. Benzo-indigo-blue yields very fine light and dark indigo-blue shades, which are fairly fast to soap, but not very fast to light. They are not affected by dilute acids, but become reddish by the action of alkalies. The fastness of the colour is increased by boiling the dyed goods with solutions of aluminium sulphate, stannic chloride, or Turkey-red oil. Salts of iron, chromium or copper have the same effect, but they make the colour duller, whereas the former substances brighten the shade somewhat.

BENZO-BLACK-BLUE G (Bayer, Levinstein).



Benzo-black-blue G is produced by combining *one* molecule of tetrazodiphenyl disulphonic acid with *one* molecule of alphanaphthylamine, diazotising the product and combining it with *two* molecules of alphanaphthol sulphonic acid N W.

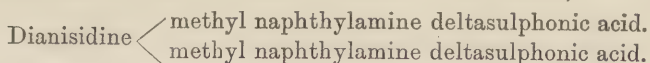
Black powder; aqueous solution, blue-black; H Cl, black-blue precipitate; Na O H, soluble black-blue precipitate; solution in H₂ S O₄, dark green; on diluting, black-blue precipitate.

Application.—Same as Congo-red. The shade is greyish-blue to black-blue, fairly fast to soap, dilute acids and alkalies, and moderately fast to light.

BENZO-BLACK-BLUE R (Bayer).

This is a product similar to the preceding, which yields dark blue-violet shades. It is obtained analogously if tetrazoditolyl (not the sulphonic acid) be used instead of tetrazodiphenyl disulphonic acid.

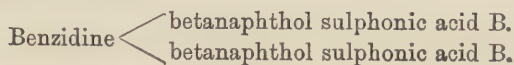
HELIOTROPE (Bayer, Berlin, Leonhardt, Levinstein).



Dark brown powder; aqueous solution, magenta-red; H Cl, violet precipitate; Na O H, soluble crimson precipitate; solution in H₂ S O₄, blue; on diluting, violet precipitate.

Application.—Same as Congo-red. Heliotrope dyes a red-violet "heliotrope" shade, which is fairly fast to washing, but not fast to light. It is slightly sensitive to dilute acids, not to alkalies. By treatment with boiling solution of copper sulphate the fastness to light and soap is greatly increased (see *Benzoazurin G*, p. 436).

CONGO-VIOLET (Berlin), **BORDEAUX COV** (Berlin), or **BORDEAUX EXTRA** (Bayer).



Brown powder; aqueous solution, claret-red; HCl , violet precipitate; NaOH , makes the solution more yellowish; solution in H_2SO_4 , violet; on diluting, violet precipitate.

Application.—Cotton is dyed with the addition of soap and phosphate of soda, or with the addition of salt only, in a boiling bath. Bluish-pink to violet shades are thus produced.

Wool is dyed in an acid bath, like the acid colours, and claret shades are obtained.

DIAMINE-VIOLET N (Cassella).

Benzidine $\begin{cases} \text{gamma-amidonaphthol sulphonic acid.} \\ \text{gamma-amidonaphthol sulphonic acid.} \end{cases}$
(combined in acid solution).

Black-brown powder; aqueous solution, red-violet; HCl , violet-black; NaOH , no change; solution in H_2SO_4 , green-blue; on diluting, red-violet precipitate.

Application.—Same as diamine fast red F (Cassella) (see p. 418). The fixation with chromium fluoride, however, offers no special advantage for this dyestuff.

Diamine-violet N produces a bright red-violet shade, which is not sensitive to dilute acids, and is fairly fast to light.

HESSIAN VIOLET (Leonhardt, Berlin, Bayer).

Diamidostilbene disulphonic acid $\begin{cases} \text{alphanaphthylamine.} \\ \text{betanaphthol.} \end{cases}$

Brown-black powder; aqueous solution, red-violet; HCl , blue precipitate; NaOH , soluble crimson precipitate; solution in H_2SO_4 , blue; on diluting, violet precipitate.

Application.—Dye cotton in a boiling bath, with the addition of 5 per cent. of borax and a small quantity of common salt; pass through soda solution and dry.

Hessian violet dyes a dull red-violet shade, which is rather sensitive to acids and not fast to light; it possesses the fastness to washing and alkalies common to these dyestuffs.

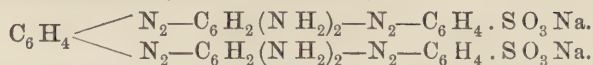
AZO-VIOLET (Bayer, Berlin, Leonhardt, Levinstein).

Dianisidine $\begin{cases} \text{naphthionic acid.} \\ \text{alphanaphthol monosulphonic acid N W.} \end{cases}$

Black-blue powder; aqueous solution, red-violet; HCl , blue precipitate; NaOH , crimson colour; solution in H_2SO_4 , blue; on diluting, blue precipitate.

Application.—Same as Congo-red.

Azo-violet yields a dull blue-violet shade, which is fairly fast to soap, dilute acids and alkalies, and moderately fast to light. By treatment with a boiling solution of copper sulphate (see *Benzoazurin G*, p. 436), the shade becomes faster to soap and light and less reddish.

BENZO-BROWN G (Bayer, Levinstein).

Benzo-brown G is produced by combining diazotised sulphanilic acid with Bismarck-brown. Dark brown powder; aqueous solution, orange-brown; H Cl, brown precipitate; Na O H, soluble brown precipitate; solution in $\text{H}_2\text{S O}_4$, black-brown; on diluting, at first violet solution, then brown precipitate.

Application.—Benzo-brown is dyed at the boiling temperature either in a neutral bath, with the addition of about 10 per cent. of common salt, or in an alkaline bath, with the addition of 5 per cent. of soda and 2 per cent. of soap. It yields a yellowish shade of brown, fairly fast to soap and to dilute acids and alkalies, but not to light.

BENZO-BROWN B (Bayer, Levinstein).

This dyestuff is produced analogously to the preceding by using naphthionic acid instead of sulphanilic acid. It shows the same reactions and properties, and is dyed in the same way. The shade is slightly less yellowish.

CONGO-BROWN G (Berlin, Levinstein).

Congo-brown G is produced by the action of one molecule of diazotised sulphanilic acid on one molecule of benzidine-azoresorcin-salicylic acid (cloth-orange—Bayer).

Brown powder; aqueous solution, red; H Cl, brown precipitate; Na O H, red colour; solution in $\text{H}_2\text{S O}_4$, red-violet; on diluting, dark red-brown precipitate.

Application.—Congo-brown is dyed in a neutral bath; it yields a yellow shade of brown which is fairly fast to soap, dilute acids, and alkalies, and moderately fast to light.

CONGO-BROWN R (Berlin, Levinstein).

This colouring matter is produced analogously to the preceding one by using naphthionic acid instead of sulphanilic acid. It shows the same reactions and properties, and is dyed in the same way; the shade is a reddish-brown.

TOLUYLENE-BROWN (Oehler).

The toluylene-browns possess a constitution similar to that of the benzo-browns and Congo-browns. For their production * toluylene-diamine sulphonic acid is diazotised and combined with metaphenylene-diamine, to form a sulphonic acid of a kind of Bismarck-brown. This compound is converted into toluylene-brown by combination with diazotised sulphanilic acid or orthotoluidine sulphonic acid or naphthylamine sulphonic acid.

Several brands of toluylene-brown (R, M, and B) are in the market.

* Kallab and Rudolph, *Journ. Soc. Dyers and Col.*, 1891, p. 19.

Toluylene-brown R is a dark brown powder; aqueous solution, brown; H Cl, brown precipitate; Na O H, soluble orange precipitate; solution in $\text{H}_2\text{S O}_4$, brown-violet; on diluting, brown precipitate.

Application.—**Cotton** is dyed with advantage in the unbleached state, as it takes up the colour better than bleached cotton. The bath is prepared with $2\frac{1}{2}$ per cent. (of the weight of the material) of oil soap, and brought to the boil; if a scum of lime soap forms on account of the water being calcareous it is carefully removed. 20 per cent. of salt and the necessary amount of dyestuff are added, and the material is entered and dyed for one hour at a temperature slightly below the boil. If desirable for shading purposes 5 per cent. of soda or potash may be added to the bath.

Toluylene-brown R yields a fine chestnut brown, toluylene-brown M and B, bluer shades of brown which are fairly fast to soap, dilute acids, and alkalies, but not fast to light.

Wool and union goods are dyed with the addition of 20 per cent. of common salt. Fine brown shades are obtained, which are fairly fast to milling.

Silk is dyed either in a bath of acidulated boiled-off liquor, or with 20 per cent. of common salt and $2\frac{1}{2}$ per cent. of acetic acid, or with the addition of 20 per cent. of salt only.

DIAMINE-BROWN V (Cassella).

Benzidine $\left\{ \begin{array}{l} \text{gamma-amidonaphthol sulphonic acid.} \\ \text{metaphenylene diamine.} \end{array} \right.$

Brownish-black powder; aqueous solution, reddish-brown; H Cl, reddish-violet precipitate; Na O H, soluble reddish-violet precipitate; solution in $\text{H}_2\text{S O}_4$, blue-violet; on diluting, brown precipitate.

Application.—**Cotton** is dyed in a boiling bath with the addition of 5 per cent. of soda ash and 15 per cent. of sodium sulphate. It may also be dyed in a neutral bath.

Silk is dyed in a neutral bath containing common salt, and is brightened in acetic acid.

Diamine-brown yields violet-brown shades, which are fairly fast to soap, light, acids, and alkalies. It can be diazotised on the fibre and combined with phenols and amines, by which process it loses the property of bleeding, while the depth of the shade is increased. (See p. 446, *Diamine ingrain colours*.)

COTTON-BROWN N (Cassella).—Composition not known.

Dark brown powder; aqueous solution, reddish-brown; H Cl, reddish-brown precipitate; Na O H, no change; solution in $\text{H}_2\text{S O}_4$, reddish-violet; on diluting, reddish-brown precipitate.

Application.—**Cotton** is dyed with the addition of 15 per cent. of sodium sulphate and 5 per cent. of potash; **Wool** with the addition of 10 per cent. sodium sulphate in a boiling bath. Cotton-brown

N yields a fine chestnut-brown shade. (See also p. 446, *Diamine ingrain colours*.)

COTTON-BROWN A (Cassella).—Composition not known.

Dark green powder; aqueous solution, reddish-brown; H Cl, dark brown precipitate; Na O H, no change; solution in H_2SO_4 , red-violet; on diluting, dark brown precipitate.

Application.—Same as cotton-brown N; the shade is bluer. (See also p. 446, *Diamine ingrain colours*.)

HESSIAN BROWN 2 B (Leonhardt).

Benzidine $\left\{ \begin{array}{l} \text{resorcinazosulphanilic acid.} \\ \text{resorcinazosulphanilic acid.} \end{array} \right.$

Hessian brown is produced by the action of one molecule of tetrazodiphenyl on two molecules of resorcinazosulphanilic acid, a yellow azo-dyestuff known as chrysoin, tropaeolin R, &c. (See p. 515.)

Dark brown powder; aqueous solution, brown; H Cl, brown precipitate; Na O H, dark red colour; solution in H_2SO_4 , violet-black; on diluting, brown precipitate.

Application.—Dye in a boiling bath with the addition of 25 per cent. of salt and 5 per cent. of potash. Hessian brown 2 B yields a red shade of brown which resembles the benzo-browns and Congo-browns in fastness to washing, acids, and alkalies.

HESSIAN BROWN 2 M (Leonhardt).

This is the derivative of tolidine, corresponding to Hessian brown 2 B, which product it strongly resembles. It dyes a bluer shade of brown.

TERRA-COTTA F (Geigy).

Terra-cotta F is produced by the combination of one molecule of diazotised naphthionic acid and one molecule of diazotised primuline with one molecule of metaphenylene diamine.

Chocolate-brown powder; aqueous solution, orange-brown; H Cl, brown precipitate; Na O H, soluble brown precipitate; solution in H_2SO_4 , brown; on diluting, brown precipitate.

Application.—Terra-cotta F is dyed on cotton with the addition of 1 part of soda, 1 part of soap, and 2 parts of salt per 100 parts of water. Dye in a boiling bath for 30 minutes, and allow to cool in the bath.

Terra-cotta F produces a fine red shade of brown, which is sensitive to acids, but not affected by alkalies; it does not resist the action of light.

MIKADO-BROWN (Leonhardt, Berlin, Bayer).

This dyestuff is produced, like the other Mikado colours, by the action of alkalies on paranitrotoluene sulphonic acid in the presence

of oxidisable substances. The constitution of the product is not known. It is sold in different shades, which show the following reactions:—

Dark brown powder; aqueous solution, brown; HCl , brown precipitate; NaOH , no change; solution in H_2SO_4 , violet-black; on diluting, brown precipitate.

Application.—Same as Mikado-orange; 100 per cent. (of the weight of the cotton) of salt are required to exhaust the bath well.

Mikado-brown yields various shades of brown, from yellowish- to bluish-brown.

BENZO-GREY (Bayer, Levinstein).

For the production of this dyestuff one molecule of tetrazodiphenyl is combined with one molecule of salicylic acid and one molecule of alphanaphthylamine, and the product, after being diazotised, is combined with one molecule of alphanaphthol sulphonic acid N W.

Greyish-black powder; aqueous solution, reddish-brown; HCl , black precipitate; NaOH , no change; solution in H_2SO_4 , blue; after diluting, black precipitate.

Application.—Cotton is dyed in a boiling bath, with the addition of 10 per cent. of common salt; if required, phosphate of soda or potash, &c., may be added to the bath.

Benzo-grey yields shades from light reddish-grey to almost black, which are not sensitive to dilute acids or alkalies.

BENZO-BLACK (Bayer, Levinstein).

This colouring matter seems to be similar to benzo-grey. It shows nearly the same reactions, and dyes shades from light bluish-grey to black.

BENZO-OLIVE (Bayer, Levinstein).

Benidine $\left\{ \begin{array}{l} \text{salicylic acid.} \\ \text{alphanaphthylamine—dioxynaphthalene sulphonic acid.} \end{array} \right.$

For the production of this dyestuff one molecule of tetrazodiphenyl is combined with one molecule each of salicylic acid and of alphanaphthylamine; the product is diazotised, and combined further with one molecule of (1 : 8) dioxynaphthalene sulphonic acid.

Black powder; aqueous solution, dark olive-green; HCl , dark green precipitate; NaOH , brown-black colour; solution in H_2SO_4 , dark violet; on diluting, dark green precipitate.

Application.—Benzo-olive is dyed on cotton in a boiling neutral bath with the addition of 10 per cent. of salt; if required, alkaline salts may be added to the bath.

Benzo-olive dyes shades from olive to Russian green, which are very fast to soap and acids, and moderately fast to light. The colour becomes brownish by the action of alkalies.

AZO-MAUVE (Oehler).

Azo-mauve has recently appeared in commerce, but nothing is known as yet about its constitution. The dyestuff seems to be related to the toluylene-browns.

Black-grey powder with a metallic reflex; aqueous solution, violet; HCl , violet precipitate; NaOH , soluble precipitate; solution in H_2SO_4 , blue; on diluting, violet precipitate.

Application.—Same as toluylene-brown. Azo-mauve dyes from pearl-grey and reddish-grey to black-violet shades, which are fairly fast to soap and dilute acids and alkalies, but not fast to light.

VIOLET-BLACK (B.A.S.F.)

Paraphenylene diamine $\left\{ \begin{array}{l} \text{alphanaphthol sulphonic acid N W.} \\ \text{alphanaphthylamine.} \end{array} \right.$

This product is prepared by combining diazoacetanilide with naphthol sulphonic acid, eliminating the acetyl-group, diazotising and coupling with naphthylamine.

Black powder with a bronze reflex; aqueous solution, brown-red; HCl , violet precipitate; NaOH , red-violet colour; solution in H_2SO_4 , blue; on diluting, violet precipitate.

Application.—Dye in a boiling bath with the addition of soap. Violet-black yields a very deep violet, almost black shade, which is fairly fast to soap and moderately fast to light.

DIAMINE-BLACK R (Cassella).

Benzidine $\left\{ \begin{array}{l} \text{gamma-amidonaphthol sulphonic acid.} \\ \text{gamma-amidonaphthol sulphonic acid.} \end{array} \right.$
(combined in alkaline solution).

Black powder; aqueous solution, violet-black; HCl , blue precipitate; NaOH , violet colour; solution in H_2SO_4 , blue; on diluting, red-blue precipitate.

Application.—Cotton is dyed in a boiling bath with the addition of 15 per cent. of sodium sulphate and 5 per cent. of soda ash or in a neutral bath.

Silk is dyed in a neutral bath or in one acidulated with acetic acid. It does not take up the colour freely from alkaline baths.

Diamine-black R yields shades from a reddish-grey to deep black-violet, and, with great amounts of dyestuff, almost black, which are fairly fast to light, soap, dilute acids, and alkalies. The dyestuff can be diazotised on the fibre and made faster to washing by combining it with phenols and amines. (See next page.)

Diamine-black R serves well as a bottom for aniline black.

DIAMINE-BLACK B (Cassella).

Ethoxybenzidine $\left\{ \begin{array}{l} \text{gamma-amidonaphthol sulphonic acid.} \\ \text{gamma-amidonaphthol sulphonic acid.} \end{array} \right.$
(combined in alkaline solution).

Black powder ; aqueous solution, black blue ; H Cl, blue precipitate ; Na O H, no change ; solution in H₂ S O₄, black-blue ; on diluting, red-blue precipitate.

Application and Properties.—Same as diamine-black R.

Diamine-black B dyes shades from steel-grey to black-blue and bluish-black, which possess the same fastness as diamine-black R.

DIAMINE-BLACK-BLUE E (Cassella).

Ethoxybenzidine $\left\{ \begin{array}{l} \text{gamma-amidonaphthol sulphonic acid.} \\ \text{betanaphthol sulphonic acid.} \end{array} \right.$

Black powder ; aqueous solution, black-blue ; H Cl, blue precipitate ; Na O H, no change ; solution in H₂ S O₄, black-blue ; on diluting, blue precipitate.

Application and Properties.—Same as diamine-black R.

Diamine-black-blue E dyes shades from bluish-grey to black-blue purer than those of diamine-black B. It is fairly fast to soap, dilute acids, and alkalis, but inferior to the two preceding diamine-blacks as regards fastness to light.

DIAMINE INGRAIN COLOURS.

A great number of direct cotton colours can be diazotised on the fibre, and combined with phenols and amines precisely similar to primuline (p. 433). L. Cassella & Co. have perfected this process for their direct blacks and browns, and thus produce shades which are not very different from the original shades except in depth, but greatly superior for their fastness to soaping, and which are free from the defect of bleeding. Some of their processes have been patented. Diamine-black R and B, diamine-blue-black E, diamine-brown and the two cotton-browns, A and N, may be used in this way with advantage.

The materials are dyed with the required amount of dyestuff as usual, and subsequently passed through the diazotising bath in exactly the same way as indicated for the ingrain colours of primuline (p. 433). They are then rinsed in cold water (which, if very hard, is neutralised with a little acetic acid) and entered *immediately* into the developing bath. The goods must not be exposed to light, exactly as is the case with the primuline colours.

The following developers give the best results :—

Blues.—Dye with diamine-black R or B, or diamine-blue-black E, diazotise and develop with *betanaphthol* for dark navy and with *naphthylamine ether* for lighter and brighter shades.

1. *Betanaphthol*.—Dissolve 51 parts of betanaphthol and 42 parts of caustic soda (75° Tw., 33 per cent. Na O H) in 44 parts of water, and heat until all is dissolved. Prepare the bath for every 1,000 litres (100 galls.) of water with 20 litres (2 galls.) of this solution, and besides 10 litres (1 gall.) more for every 100 kgs. (100 lbs.) of material (the first lot included). The bath is used continuously. Turn a few times in the bath, rinse and dry.

2. *Naphthylamine Ether*.—This product is supplied ready for use in the form of a paste. Start the bath with 9 kgs. (9 lbs.) of the paste dissolved in 100 litres (10 galls.) of boiling water for every 1000 litres (100 galls.) For freshening up, use 5 kgs. (5½ lbs.) in 50 litres (5 galls.) of boiling water for every 100 kgs. (100 lbs.) of material. Turn a few times in the bath, soap hot, rinse, and dry.

Blacks.—Dye with diamine-black R or B, diazotise and develop with phenylene-diamine, resorcin, or a mixture of resorcin and betanaphthol.

1. *Phenylene-Diamine*.—This developer is supplied by the makers of the colours both in the form of a solution ready for use and in the solid state, with instructions how to prepare the solution. It is used in the same way as the solution of betanaphthol.

2. *Resorcin*.—Dissolve 39 parts of resorcin and 84 parts of caustic soda (75° Tw., 33 per cent. NaOH) in 44 parts of water, and heat until all is dissolved. Use this solution in the same way as the naphthol solution. Both may be used together in the same bath. Develop as usual.

Browns.—*Chrysoidine A G* (Cassella), is recommended as the best developer for diamine-brown V, and cotton-browns A and N.

Prepare the bath with 125 grms. (2 oz.) of chrysoidine for every 1000 litres (100 galls.) of water, and add another 440 grms. (7 oz.) of chrysoidine for each lot of 100 kgs. (100 lbs.) of material to be developed (the first lot included). Keep the bath neutral by adding 550 grms. (9 oz.) of ground chalk for each lot of 100 kgs. (100 lbs.) of material. Turn a few times, soap hot, rinse, and dry. Still better results are obtained by developing once, rinsing in water, developing again, hot soaping, rinsing, and drying.

The ingrain shades are fuller than those which can be produced with diamine-colours alone and possess the great advantage of not bleeding; moreover they are very fast to rubbing and dilute acids and resist the light pretty well. They are also suitable as bottoms for aniline-black and indigo-blue, and, finally, they are capable of serving as mordants for the basic dyestuffs, retaining the property of the direct cotton colours to form lakes with them.

Recently it has been recommended to dye and develop the blacks on a bottom of aniline-black; by this method a fast black is produced without injuring the fibre. (See *Aniline-black*.)

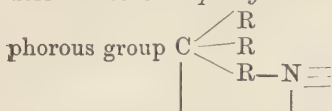
BASIC COLOURS.

The basic colours are the salts of organic bases of artificial origin. Their colour-bearing or chromophorous group is contained in the bases, hence the name, "basic colours." The bases in the free state are colourless, and their chromogenous character appears only when they

combine with acids to form salts. In the dyeing of the various textile fibres the dyestuff-salts present in the dye-bath are decomposed; the acid remains in solution, while the colour base combines with an acid already present in or on the fibre, and thus gives rise by chemical action to a real coloured insoluble, or sparingly soluble, salt or lake, which forms the dye. In the case of the vegetable fibres, cotton and linen, this acid must be deposited in the fibre by mordanting with tannic acid, Turkey-red oil, &c., whereas the animal fibres act by themselves as acids: hence they are dyed without mordants. Jute behaves like tanned cotton.

All the basic colours have the property of dyeing cotton mordanted with tannin or other acid-mordants—*e.g.*, Turkey-red oil or soap—and the same dyestuff always assumes on the different mordants a more or less similar shade. Even the shade is not materially altered if any of the acid-mordants is fixed by different metals, either antimony, or tin, or aluminium, &c. Hence these dyestuffs are *monogenetic*.

The basic colours vary greatly in their general physical and chemical properties, in their constitution and their chromophors, and, lastly, in the brilliancy and fastness of their shades. A large number, like magenta, malachite-green, rosaniline-blue, and methyl-violet are derivatives of *triphenylmethane* and are characterised by the chromo-

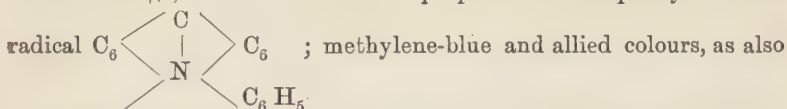


They are distinguished from most of

the other basic colouring matters by superior beauty, but associated with great fugitiveness. Many of the basic colours, like the safranines, new blue, and the indulines are azine-derivatives, containing the

colour-bearing group $\text{C}_6 \begin{array}{c} \diagup \text{N} \\ | \\ \diagdown \text{N} \end{array} \text{C}_6$; still others, like phosphine and

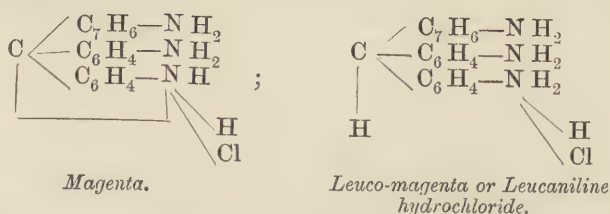
acridine-orange, owe their tinctorial properties to the phenyl-acridine



thioflavine, contain sulphur as an essential constituent; and, lastly, chrysoïdine and Bismarck-brown are azo-colours.

All the basic colours are decolorised by reducing agents, like tin and hydrochloric acid. In the case of the two last named azo-colours a disruption of the molecule takes place, chrysoïdine being converted into aniline and triamidobenzene, whilst Bismarck-brown yields meta-phenylene diamine and triamidobenzene. Almost all the other basic colours are converted by the action of nascent hydrogen into colourless so-called *leuco-compounds* (*i.e.*, white compounds, from the Greek word *leukos* for "white") which contain two atoms of hydrogen more than the original substances, and are, in most cases, readily reconverted into the

dyestuffs by oxidising agents, often simply by the action of atmospheric oxygen.



The basic colours are brought into commerce generally as salts of hydrochloric acid; some as acetates, oxalates, sulphates, nitrates, or as double salts of hydrochloric acid and zinc chloride; in rare cases in the form of the colour base in the free state. They are sold as powders, crystals, or pastes. Most of the basic colours are soluble in water, while all dissolve in alcohol. On addition of the hydroxides or carbonates of the alkalis and alkaline earths to the solutions, in most cases, the colour bases are thrown down in the free state, most of them being insoluble in water.

If the water used in dyeing contains considerable quantities of carbonate of calcium or magnesium (*i.e.*, if it shows great temporary hardness) it acts on the colour by throwing down the colour base in the form of a curdy precipitate, and thereby rendering a part of it useless for dyeing purposes; while further injury may be done by the precipitate being deposited on the goods, thereby giving rise to spots and unevenness. If the alkalinity of the water is neutralised by the addition of acid this does not take place.

The following experiment is very instructive:—If equal weights of wool are dyed with equal quantities of dyestuff dissolved in one case in distilled water, and in the other in calcareous water, the material acquires a greater depth of colour in the former bath than in the latter. If each bath has been entirely decolorised by the wool, the first remains colourless on the addition of acid, being thoroughly exhausted; whereas in the second bath the colour distinctly reappears; in this latter case that part of the dyestuff which has been precipitated in the form of the colourless base becomes visible by being changed into the coloured salt, and passing into solution. Hence it is often advisable, especially in the case of wool and silk, to dye in a slightly acidulated bath; an excess of acid, however, prevents the bath from being exhausted.

It has already been stated that the wool fibre acts as an acid towards the basic colours, and in the light of this fact we can understand the behaviour of wool and dyestuffs towards each other. In an alkaline bath—*i.e.*, in one containing much calcium carbonate—the wool fibre readily takes up all the colouring matter which is present in solution, both free and combined; but that part which is not dissolved is only gradually attracted. In neutral, or slightly acid baths, the acidity of

the wool fibre is strong enough to decompose the colour salt and to combine with the bases. A large amount of acid in the free state, however, prevents, more or less, the formation of the compound between the fibre and the base; hence strongly acid baths are not exhausted.

The basic colours are distinguished by great tinctorial power and, generally, by their purity and brilliancy of shade which, amongst dyestuffs, can only be matched by those of the eosins, rhodamines, and very few of the other artificial colouring matters (*e.g.*, resorcin-blue). These great advantages are largely counterbalanced by their fugitiveness to light and their limited fastness to soaping and milling. Some, like methylene-blue and the indulines, it is true, are considerably faster than the rest. An attempt has recently been made to impart to the basic colours greater fastness to light by treating the dyed goods with a solution of copper sulphate, which process gives excellent results with other dyestuffs (*e.g.*, benzoazurin); but the great alteration of shade precludes this process being generally adopted.

A number of basic colours are transformed by the action of strong sulphuric acid into sulphonic acids and are thereby converted into acid dyestuffs. The shades of the latter are similar to those of the mother substances, but in their other dyeing properties they are thoroughly changed, while their tinctorial power is greatly reduced.

By the following method it can be determined whether a dyestuff belongs to the basic colours or not:—

Prepare a solution of 20 grms. (1 oz.) of picric acid and 50 grms. (3 oz.) of sodium acetate in 1 litre (3 pints) of water; or dissolve 100 grms. (3 oz.) each of tannic acid and of sodium acetate in 1 litre (1 quart). Of either solution add a few drops to the clear solution of the dyestuff in question, and heat gently; either reagent forms a precipitate with basic colours, whereas the solutions of other dyestuffs remain clear. To detect basic colours on the fibres, the material may be treated with caustic soda (so as to separate the colour-base in the free state), subsequently washed with water, and dried; the colour-base is then extracted with ether, the latter evaporated, and the colour-base finally dissolved in water containing the necessary amount of acetic acid to form a salt. The solution can then be examined as indicated, or tanned cotton may be dyed in it.

The basic colours were the first artificial or so-called aniline colours introduced on a large scale into commerce. They have rapidly won the favour of the public by the great beauty of their shades, and they are used even to-day in large quantities, in spite of the many other dyestuffs invented during the last 25 years, many of which are either faster to light or less expensive. They are more or less replaced by the direct cotton colours in the dyeing of cotton goods when the property of the latter to "bleed" is not injurious; but they are used still in large quantities in calico-printing. In wool-dyeing they have

been almost superseded by the various colours which are dyed in acid baths, while they are still of great importance to the silk-dyer whose customers desire fine tints without regard to fastness.

Methods of Dyeing with the Basic Colours.—The basic colours are dyed in neutral or slightly acid or sometimes in alkaline baths. Hard water is corrected by the addition of acid; in the case of cotton and silk, acetic acid is generally used; for wool, hydrochloric or sulphuric acid, bisulphate of soda, and alum are employed, in addition to acetic acid. A great excess of acid in the dye-bath must, however, be avoided, as it prevents its complete exhaustion.

On account of the great tinctorial power of many basic dyestuffs, small quantities are sufficient to produce full shades. Magenta and others give full shades with 1 per cent., and medium shades with $\frac{1}{3}$ to $\frac{1}{2}$ per cent. of dyestuff. For dark blues 3 per cent. of dyestuff and even more are necessary.

In contrast to the direct cotton colours, the basic colouring matters are almost completely taken up from the dye-bath unless a large amount of dyestuff be used or the bath be too acid or alkaline. All the basic colours can be mixed and dyed together in one bath to produce compound shades; but they will not always be attracted by the fibres equally well.

Dissolving the Colours.—The basic colours must be dissolved with special care. It is best to use condensed water, or water which has been slightly acidulated with acetic acid. The most suitable temperature is 80°, since some dyestuffs (*e.g.*, auramine) do not stand a boiling heat. The best method of dissolving is to pour hot water over the colour, and then to stir well, or to dissolve the colour with water in a steam-jacketed pan with frequent stirring (not directly over a fire). Generally the basic colours require about 250 times their weight of hot water for solution. If the solution has been standing for some time, and any of the colour has crystallised out on cooling (magenta and auramine being most liable to do this), the dyestuff is redissolved by warming and stirring; it is better, however, to avoid it by dissolving as much colour as is required for immediate use only.

Colours which are insoluble in water are dissolved in dilute alcohol in a closed pressure boiler on a water-bath or steam-bath. In an open vessel loss of alcohol from evaporation would result. About 50 parts of methylated spirits and 50 parts of water are required for 10 parts of colour.

For printing purposes the solutions are often prepared in different ways.

The colours are filtered through cotton, flannel, or a hair-sieve before being used, in order that no undissolved parts may pass into the dye-bath and soil the goods.

Dyeing of Cotton with the Basic Colours.—Before dyeing, the

cotton is well boiled in soda ash, and, for light and brilliant shades, it has also to be bleached; for dark indigo, brown, and black shades, bleaching is not requisite. Some of the basic colours (*e.g.*, safranine, methylene-blue, and Bismarck-brown) dye light shades on unmordanted cotton; this is taken advantage of for producing delicate tints on bleached cotton; but the shades thus obtained are not fast. A very few colours of the induline class (*e.g.*, toluylene-blue and Malta-grey) yield full and fast colours on unmordanted cotton by a treatment in bichromate of potassium after dyeing. Generally the cotton must be prepared, however, with mordants before being dyed with the basic colours.

The methods of mordanting may be classed as follows:—

- (1) Mordanting with tannins;
- (2) Mordanting with Turkey-red oil or soap;
- (3) Previous dyeing with other dyestuffs which serve as mordants.

The sulphides of zinc and tin are capable of acting as mordants for the basic colours; and, less effectively, sulphur. The zinc salts of hydroferrocyanic and hydroferricyanic acids (*i.e.*, the precipitates of zinc salts with yellow and red prussiate of potash) have also been proposed as mordants.*

(1) *Tannin-mordants*.—The tannic acids form lakes with the basic colours, which are insoluble in water, but dissolve in excess of tannic acid. Hence the colours are not fixed well and are not fast to washing on the tannins alone. The tannin, however, can be converted, as previously explained (p. 180), by various metals into insoluble compounds, which also have the power of forming lakes with the basic colours, but do not dissolve them.

The metals used for this purpose are antimony, tin, iron, and aluminium; zinc and chromium have also been proposed, but offer no advantage. None of the other metals can compare in importance as fixing agents with antimony, which imparts the greatest fastness to light and to soap. Tin is inferior as to fastness; but the colours are taken up less rapidly and dye more evenly; it is also cheaper. Iron produces dark and dull shades; and aluminium is used only in special cases.

The solutions of the tannin-lakes of the basic colouring matters are, as a rule, duller than the solutions of the pure colour salts. This explains how it is that when dyed on tanned cotton they are not so bright as on wool or silk or on oil-mordanted cotton.

The modes of mordanting and fixing are referred to in the chapters describing the materials. For light and medium shades 2 to 5 per cent. of tannic acid (of the weight of the cotton) is used; for dark shades the amount required rises to 10 per cent. For the latter, sumach or gallnuts, &c., can be employed with advantage (5 to 10 times as much as tannic acid would be necessary, according to quality); but pure

* Balanche, *Journ. Soc. Chem. Ind.*, 1882, p. 182; C. Reber, *ibid.*, 1885, p. 343.

light shades cannot be obtained with ordinary tannin materials, on account of the reddish colouring matters they contain. With the best qualities of *decolorised* sumach extracts delicate tints can be produced.

Note.—In the following the term “tannin” will be used to denote all kinds of tannin-mordants, leaving it to the judgment of the dyer whether he shall select tannic acid, sumach, decolorised extracts, or any other. The quantities refer to tannic acid (gallotannic acid) unless otherwise stated.

The cotton is steeped in the solution of tannin-mordant at a temperature not much higher than 60°, and left in the bath for some hours or overnight; it is then slightly rinsed in cold water, and either dyed directly or passed into the fixing bath.

The tannin-bath can, with fresh additions of tannin, be used continuously until it becomes too dirty. (See p. 176.)

For fixing with antimony the various antimony salts described can be employed. About $\frac{1}{2}$ to 3 per cent. of tartar emetic (or corresponding quantities of other antimony salts) and the indicated amounts of soda are used; the bath is kept of such a strength as to contain about 10 to 20 grms. of tartar emetic per litre (1 to 2 lbs. per 10 galls.), and is used at a temperature of about 30° to 50°. The baths are also used continuously and their strength is restored from time to time, while the acid produced in the fixing process is carefully neutralised.

The cotton must be washed very carefully after having been treated with antimony, since superficially fixed antimony will not only give rise to rubbing of the ultimate colour, but is liable to affect the skin and to produce blood-poisoning. For the dyeing with some colours (*e.g.*, methylene-blue and Victoria-blue) the washing with water alone is not sufficient to obtain even shades. The cotton is in this case worked for 20 to 30 minutes in a warm soap-bath containing per litre (10 galls.) $1\frac{1}{2}$ grms. ($2\frac{1}{2}$ oz.) of neutral soap. It is finally made ready for dyeing by a thorough washing in water. This soaping is generally of advantage for the production of clear and even shades. The risk, both of rubbing and poisoning is lessened, and the fastness to washing and milling increased by passing the *dyeed* goods anew through a tannin-bath; the excess of antimony is fixed by this after-treatment. The goods must be rinsed again in water when thus tanned after dyeing, as an excess of tannin would soil the shade. This second treatment with tannin is also of good service, if metals other than antimony are used as fixing agents.

For the fixation with tin, stannic chloride (see p. 288), or in certain cases stannous chloride, is used.

Iron is employed in the form of various salts (copperas, pyrolignite of iron, nitrate of iron). It is of advantage to pass the goods after the treatment with iron through very weak lime water. Sometimes the cotton is treated with iron salts, after having been mordanted with tannin and antimony, to obtain greater fastness to washing, or it is *adened*, after dyeing, in basic nitrate of iron (see pp. 275-277).

Aluminium is used in the form of basic alum or aluminium acetate ; in either case of 1° to 2° Tw. (see pp. 233 and 234).

The fixation with zinc has not found favour with dyers. It has been recommended to use a bath containing about 10 grms. (1 lb.) of zinc sulphate and 5 grms. ($\frac{1}{2}$ lb.) of sodium acetate per litre (10 galls.).

When cotton pieces are worked on a jigger the processes of tanning and fixing are generally the same ; but much stronger liquors are used in order to shorten the time required to incorporate the materials with the fibre.

(2) *Turkey-red Oil and Soap as Mordants.*—These two materials act like tannic acid by their acid constituents as mordants, and are also fixed on the cotton, before dyeing, in the form of more or less insoluble metallic salts. They yield shades which are brighter than those produced with tannic acid, but are not at all fast to soaping, while they are very fugitive to light. The mode of operation is as follows:—For 10 kgs. (10 lbs.) of cotton prepare a bath with 20 litres (2 galls.) of water and 2 kgs. (2 lbs.) of Turkey-red oil or neutral soap. Soak the cotton in small portions in this bath 3 or 4 times for 2 to 3 minutes, wring out, and dry at a moderate heat ; subsequently, work the cotton at 50° for half an hour in a bath containing in 100 litres (100 galls.) about $\frac{1}{2}$ litre ($\frac{1}{2}$ gall.) of aluminium acetate (8° Tw.), wash, wring out, and work once more in a weak soap bath, 1 gr. (1 lb.) of neutral soap in 1 litre (100 galls.) of water ; finally, wash thoroughly and dye.

(3) *Colouring Matters as Mordants.*—The basic colours can be used with good results in topping other colours. As we have seen in the preceding chapter, the direct cotton colours are topped with the basic dyestuffs, and thus both may become fast to washing. Numberless compound shades can be produced in this way. The basic colours are also used to brighten the shades obtained with alizarins, logwood, and aniline-black, by topping. We might mention here the dyeing, first, with catechu, and, subsequently, with basic colours, although catechu may be considered as a tannin-mordant. In these cases the first dyestuff, or the dyestuff together with the mordants by which it has been fixed, act as acids towards the colour-base, and bind it on the fibre.

Process of Dyeing Proper.—However the cotton may be prepared, it is always dyed by the following method :—A separate bath is used to which the colour is added, during the dyeing, in small portions, in order to effect level dyeing. If the colour is apt to dye uneven, an addition of some acetic acid will cause it to go more slowly and evenly on to the fibre. The cotton is entered into the dye-bath at, or a little above, the ordinary temperature, and the dyeing may be finished, without heating, in from 30 to 60 minutes. By raising the temperature to 50° to 60° C. the colour is fixed somewhat better, but further heating is of no use, as a rule, and often the shade loses thereby in brilliancy. After dyeing, the material is wrung out, or hydro-extracted, and dried.

Rinsing in water after dyeing may be dispensed with; it is certainly not advisable, unless the goods were mordanted with tannin and subsequently with a metallic salt. As has been explained on p. 453 a treatment of the dyed goods with tannin makes the colour still faster to soaping and rubbing.

The basic colours, with a few exceptions, are not at all fast to light and not very fast to soap. Their shades, when produced on tannin in combination with metallic salts, lose by soaping more in depth than the direct cotton colours; but they are not liable to tinge the white fibres in contact with them; hence they are more suitable for calico-printing than the latter.

On tannin-mordants which have not been fixed with metallic salts and on the other mordants the basic colours are not at all fast either to soap or to light.

Dyeing of Linen with the Basic Colours.—Linen is mordanted and dyed with the basic colours exactly like cotton; but it must be freed previously from all adhering impurities by repeated bowking under pressure and by bleaching. The basic colours are not very important for the dyeing of linen, since for this fibre permanent shades are required.

Dyeing of Jute with the Basic Colours.—Jute does not require any mordants. It is dyed without any additions in boiling baths, or, when the colour does not allow of boiling, as is the case with auramine, at as high a temperature as permissible. After dyeing, jute is washed and dried.

Dyeing of Wool with the Basic Colours.—Wool has great affinity for the basic colours. It attracts them readily from their neutral solutions; hence it is easily dyed with them in a neutral bath. In very hard water, however, the colour base is precipitated in a sparingly soluble form, as explained above (p. 449), and is not taken up by the wool fibre so readily as in the form of a salt. Wherever possible, the bath is slightly acidified with acetic, hydrochloric, or sulphuric acid, sodium bisulphate, or alum. An excess is avoided, since it prevents the complete exhaustion of the bath.

In dyeing with methyl-green, and to some extent in dyeing with the benzaldehyde-greens, the bath is not exhausted as well by ordinary wool as by wool which has been mordanted with sulphur (*cf.* p. 472). A satisfactory explanation of this fact has not been found.

Wool is dyed with the basic dyestuffs according to two methods.

First method.—The dye-bath is made slightly acid and the colour solution added; if the colour is apt to dye uneven, the wool is entered at a moderate temperature, which is gradually raised, otherwise the wool may be entered into the boiling bath. After 15 to 30 minutes working at the boil, the temperature is allowed to fall to from 60° to 70°, the wool is taken out, washed without much delay, and dried. Brighter shades are obtained by cooling the wool still further in the

dye-bath ; a part of the liquor is run off and cold water is added, until the temperature has been lowered to 40° ; a small amount of neutral soap is then added to the bath and the wool turned for 10 minutes, washed, and dried.

Second method.—The dye-bath is not acidulated, and 2 to 4 per cent. of soap may be added to make the shade brighter ; but, then, the bath is not exhausted and should be kept for further use. The dyeing proceeds as by the first method.

Certain colours (*e.g.*, the benzaldehyde-greens and Victoria-blues) must be dyed in acid baths. The addition of soap to a dye-bath prepared with double salts of zinc (in which form certain colours are sold) is injurious, as it causes the formation of a sticky zinc soap.

A number of basic colouring matters are dyed by different methods, which will be described in the special part of this chapter.

The basic colours are not quite so fugitive to light on wool as on cotton. In fastness to milling they vary exceedingly ; some are very fast, while others are stripped from the fibre and tinge the white in contact with them. They are not fast to acids (carbonising), chlorine, or stoving.

Dyeing of Silk with Basic Colours.—Silk attracts the basic colours even more readily than wool, and evinces a stronger acid character towards the colour bases than the latter ; thus methyl-green and the benzaldehyde-greens are more easily taken up by the unmordanted silk fibre than by wool.

Silk is dyed with the basic colours in a neutral or alkaline bath or in one slightly acidulated with acetic, tartaric, or sulphuric acid. Water alone or soap solution or “boiled-off liquor” is used in dyeing. $1\frac{1}{2}$ to 2 per cent. of neutral soap (of the weight of the silk) or 10 per cent. of boiled-off liquor (of the volume of the dye-bath) are used. When silk is dyed in acidulated water, *i.e.*, without the addition of soap or other chemicals, about 3 grms. ($1\frac{1}{2}$ oz.) of acetic or tartaric acid are used for every 10 litres (10 galls.) of (pure) water ; and when it is necessary to dye in acidified boiled-off liquor, sufficient sulphuric acid is added to impart a distinctly sour taste and an acid reaction. The colour solution is added, gradually or at once, to the dye-bath ; the silk is entered at a moderate temperature and turned frequently, while the liquor is slowly heated to 60° or 80° or sometimes to the boil. Exact instructions will be found for each colour. After dyeing, the silk is thoroughly washed in water and then usually passed through a very weak acid bath for *brightening*. Colours which have been brightened with inorganic acids are liable to change on exposure to the atmosphere ; it is best to use solutions of about $1\frac{1}{2}$ grms. ($\frac{1}{4}$ oz.) of acetic or tartaric acid per 10 litres (10 galls.) of water. After the brightening the silk is wrung out or hydro-extracted and dried.

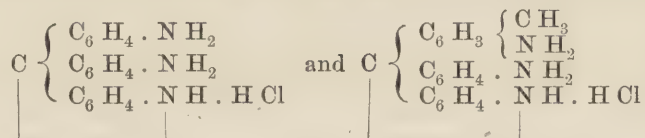
Dyeing of Mixed Goods with the Basic Colours.—*Union goods* (cotton and woollen mixed goods) can be dyed with the basic colours.

The cotton fibre is first mordanted, as described for cotton goods, with tannin and antimony, &c.; but the temperature of the tannin-bath must not exceed 45° ; if it does, the wool fibre takes up some tannin and the cotton comes out too light a colour. The dyeing is effected in a neutral or slightly acid bath; the goods are entered at about 40° and the temperature is gradually raised to the boil. Since it is better to dye wool with acid colours, dyers generally prefer to treat union goods first in a bath with acid colours so as to dye the wool fibre (sour dyeing), wash, mordant below 45° , and then to dye the cotton cold in a fresh bath with basic colours until the shade is uniform. Although wool evinces little affinity for the basic colours in cold solutions it is dyed by them to some extent; hence the full depth of shade desired should not be given to the wool fibre with the acid colours, since it is somewhat deepened in the second dye-bath.

Half Silk Goods (Satin).—Many colours do not dye well on silk which has been impregnated with tannin. For this reason half-silk goods are first dyed with basic colours by the methods given for silk dyeing so as to dye the silk fibre; and, subsequently, they are mordanted with tannin, &c., and cotton-dyed at as low a temperature as possible. The same precaution has to be observed, as in the case of "sour-dyeing" of union goods, not to dye the silk a deeper shade than desired. Another method of dyeing satin goods with basic colours is carried out in the following manner:—The material, consisting of raw silk warp and cotton weft, is first mordanted with tannin and stannic chloride (24° Tw.), then boiled-off in the usual way with soap, and both fibres dyed in one bath. The silk is thus weighted.

Silk-warp worsteds can be dyed in one bath with basic colours; but other dyestuffs are preferable.

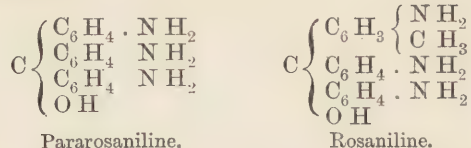
MAGENTA or **FUCHSINE**.— $C_{19}H_{18}N_3Cl$ and $C_{20}H_{20}N_3Cl$:



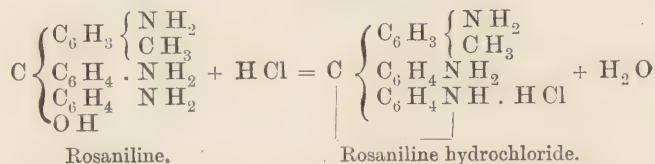
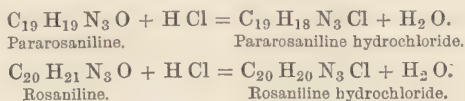
Magenta was brought into commerce as early as the year 1859, when it surprised and delighted the world by its brightness, purity, and richness of colour. It has been offered to the trade under a great many other names, as *Aniline-Red*, *Rubine*, *Roseine*, *Azaleine*, *Solferino*, &c., but at the present time it is generally sold under the names of *magenta* or *fuchsine* only.

Various brands are met with in commerce, the purest of which are those of blue shade (extra, double refined, diamond crystals); even these are not chemically uniform substances, but mixtures of the salts of two homologous bases, pararosaniline and rosaniline, which are derivatives of triphenylmethane and tolyldiphenylmethane respectively.

Pararosaniline is triamidotriphenylcarbinol and rosaniline is triamidotolyldiphenylcarbinol.



Pararosaniline and rosaniline form magenta by combining with hydrochloric acid, as shown by the following equations:—



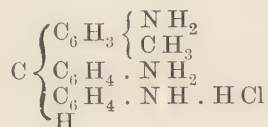
The properties of pararosaniline and rosaniline differ little; rosaniline is present in greater quantities in the commercial product than pararosaniline, and for simplicity's sake we shall mention in the following only rosaniline; but by this name we imply mixtures of rosaniline and pararosaniline.

Rosaniline base—i.e., rosaniline in the free state—is precipitated from the hot concentrated solutions of rosaniline salts on addition of caustic alkalis or alkaline earths. It forms almost colourless leaflets, which are very sparingly soluble in water, but dissolve freely in alcohol.

Rosaniline is decomposed by strong oxidising agents, such as chlorine, chloride of lime, or permanganate of potash.

Under the influence of reducing agents, rosaniline loses oxygen, and is converted into *leucaniline*: $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O} + 2\text{H} = \text{C}_{20}\text{H}_{21}\text{N}_3 + \text{H}_2\text{O}$.

The constitution of *leucaniline hydrochloride* is shown by the formula—



Leucaniline and its salts are colourless, as is indicated by the name (see p. 448). Leucaniline is stable in the air; by strong oxidising agents it is reconverted into rosaniline. Rosaniline in the free state is colourless, and its colouring character appears only when it combines with *one* equivalent of acid to form a salt like $\text{C}_{20}\text{H}_{20}\text{N}_3\text{Cl}$. It forms also diacid and triacid salts. The polyacid salts, especially the triacid salts, like $\text{C}_{20}\text{H}_{19}\text{N}_3(\text{H Cl})_3$, are very soluble in water,

and are colourless or of a brownish-yellow colour, both in the solid or dissolved state, and when fixed on the fibre. The polyacid salts are dissociated by water, forming monacid salts and free acid. The monacid salts of rosaniline, which consist of one equivalent of rosaniline and one equivalent of acid, like $C_{20}H_{19}N_3, HCl$, form crystals which have a metallic green lustre in reflected light; in transmitted light and in thin layers they are red; the solutions are crimson-red, and show no fluorescence.

Neither rosaniline nor the rosaniline salts are poisonous.

Rosaniline hydrochloride, $C_{20}H_{19}N_3, HCl$, forms rhombic crystals, which are sparingly soluble in pure water, but more readily in acidulated water or in alcohol, also amyl alcohol. The crystals absorb moisture from the air. With strong hydrochloric acid they form the triacid salt mentioned above, which is decomposed into the original salt when mixed with an excess of water.

Rosaniline acetate, $C_{20}H_{19}N_3, C_2H_4O_2$, is the most soluble rosaniline salt; it forms large green crystals, which become brownish-red after some time.

In addition to these two salts rosaniline nitrate, $C_{20}H_{19}N_3, HNO_3$, and rosaniline sulphate, $(C_{20}H_{19}N_3)_2, H_2SO_4$, are sometimes brought into commerce.

Commercial magenta is obtained on the large scale by the oxidation of the so-called *aniline-oil for red* which is a mixture of aniline, ortho-toluidine, and paratoluidine; the presence of a certain amount of paratoluidine in this mixture is necessary. The oxidising agents employed are arsenic acid (arsenic acid-process) or nitrobenzene in the presence of iron and hydrochloric acid (nitrobenzene-process). The former method has been relinquished to a great extent, and magenta is now manufactured almost exclusively by the nitrobenzene-process. The crude product contains, in addition to rosaniline and pararosaniline, phosphine and a number of inferior dyestuffs; it is purified by crystallisation, and the crystals are selected and separated according to purity; the mother liquors yield inferior qualities. In this way the various brands of commerce are obtained.

Magenta, blue shade (extra, double refined, diamond rubine), is almost pure hydrochloride of rosaniline (and pararosaniline), nearly free from phosphine or other dyestuffs.

Magenta, yellow shade, contains some phosphine. It is not easily distinguished by its appearance from magenta, blue shade, except by a dye-trial.

Impure products, which contain more phosphine, and, in addition, brownish colouring matters, are brought into commerce as amorphous powders or lumps of irregular shape, and sold under various names, as *Cerise, Grenadine, Cardinal, Amaranth, Geranium, Russian Red, Maroon, &c.*

Commercial magenta forms green crystalline masses or powders

with a metallic lustre; good qualities are always well crystallised and dissolve without leaving any considerable residue in pure water, but more readily in slightly acidulated water. The solution is almost entirely decolorised by sulphur dioxide, whereas impure samples remain dark yellow to brown when treated with this reagent. If the sample is pure the rosaniline-base is precipitated from the solution in a colourless state.

Magenta shows the following general reactions:—It dissolves in water with a bluish-red colour; hydrochloric acid turns the colour of the aqueous solution an orange-yellow; the original colour is restored by sodium acetate. Caustic soda precipitates from the aqueous solution a more or less reddish precipitate. In concentrated sulphuric acid magenta dissolves with a brownish-yellow colour; the solution becomes nearly colourless on dilution with water.

Magenta is tested by comparative dye-trials. For the detection of arsenic in magenta a sample is incinerated with soda ash and the residue tested by Marsh's test, or it is distilled with hydrochloric acid and ferrous chloride, and examined in Marsh's apparatus. In order to estimate arsenic quantitatively, magenta is fused with nitre and soda ash and the quantity of arsenic estimated by means of magnesia mixture in the form of magnesium ammonium arsenate. (See also *Analysis*, Part XI.)

Applications.—Magenta is used for the dyeing of the textile fibres, and for other materials, such as leather, paper, &c. To dissolve the crystals more readily they are ground to a powder and moistened with methylated spirits; a great quantity of water (200 to 300 parts) is required for the solution of the dyestuff; and, if the solution has been allowed to stand for some time after filtering, it should be carefully examined in order to see if any crystals have been formed.

Cotton can be dyed with magenta according to the various methods described for the basic colours. The most permanent shades are obtained on material prepared with tannin and metallic fixing agents (antimony, tin, &c.).

Cotton is mordanted with tannin and antimony or with tannin and stannic salt, and dyed in a fresh tepid bath for 45 to 60 minutes. For a full shade about 1 per cent. of dyestuff (of the weight of the material) is required. To ensure level dyeing the colour solution is added gradually. The bath is exhausted if small quantities of dyestuff are employed. After dyeing, the cotton is dried without washing. The shade thus obtained is fairly fast to soaping, but not to light. Mordanting with Turkey-red oil or soap and aluminium salts, and dyeing as on tannin-mordants, yields brighter though not fast shades. Magenta can also be fixed on cotton with albumen, but this process is altogether too expensive. Saturate the cotton with a solution of 1 to $1\frac{1}{2}$ kgs. (1 to $1\frac{1}{2}$ lbs.) of egg albumen in 50 litres (5 galls.) of water, and pass it through boiling water; dye in a cold

solution of magenta. Unmordanted cotton can also be dyed by being worked in a strong solution of magenta, to which, towards the end of the operation, some alum is added; the colour is readily stripped from the fibre by soaping and even by rinsing in water. This method is sometimes employed for producing bright tints on bleached calico, but only in cases where fastness is not required. It is said that the Chinese peasants use magenta and other colours in this way, even without adding any alum.

It has been previously mentioned that the direct cotton colours can be topped with magenta.

Wool is dyed with magenta without any preparation after scouring. The bath is slightly acidulated with acetic or sulphuric acid; sulphuric acid makes the shade more bluish than acetic acid. An addition of a quantity of magnesium sulphate (8 per cent.), or zinc sulphate (6 per cent.), or alum (3 per cent.), or Glaubersalt (20 per cent. of the weight of the wool), causes the colour to go on to the fibre more evenly and gives more brightness to the shade. The wool is dyed in a boiling bath with or without any of these additions; the boiling is continued for 15 to 20 minutes, and then the temperature is allowed to fall to 60° or 70° C., as indicated in the introduction to the basic colours (p. 455).

For a full shade about 1 per cent. of dyestuff is required; the bath is completely exhausted. The shade is not fast to milling, and, therefore, magenta is not a suitable colour for yarns which have to be milled.

Magenta is not dyed on wool as much as formerly, having been replaced by colours which either give better results or are obtained at a lower price, especially by the acid colours, such as acid magenta, fast red, &c.

Silk is dyed with magenta in a fresh soap-bath containing 1½ to 2 per cent. of neutral soap (of the weight of the silk). The liquor should lather slightly when stirred up, and, if the surface of the bath becomes bronzy during the dyeing, soap must be added until the bronze scum disappears. Turn the silk at first three times in the soap-bath; then add the colour by degrees in small quantities, and turn the silk while raising the temperature to 70° or 80°. Take the silk out when the desired shade is obtained, rinse well, brighten with acetic or tartaric acid, and dry. Mineral acids in the brightening bath produce a bluer shade, which is liable to change on exposure to the air. Magenta can also be dyed on silk in an acid bath: wash the silk in tepid water to remove any soap, and dye in a warm bath containing acetic or tartaric acid; add the colour gradually until the desired shade is obtained, and dry without washing.

Mixtures of Magenta are met with in commerce under various names. A mixture of magenta and phosphine is known as *magenta-scarlet*.

Impure Magentas: Cerise, Grenadine, Cardinal, Amaranth, Geranium, Russian Red, Maroon, &c.—These are products pre-

pared from the mother liquors of magenta crystals; and consist of mixtures of salts of rosaniline, pararosaniline, phosphine, chrysaniline, mauvaniline, violaniline, &c. They all yield duller and more yellowish shades than magenta, and are used for their comparative richness of colour, not for the brilliancy and purity of their shades.

The impure magentas are applied in dyeing exactly like magenta; but the solutions should be filtered with great care before use, since they contain much tarry matter.

Like magenta they are not fast to light.

Cerise, Grenadine, &c., are amorphous brown masses with a vitreous fracture, or powders of a brown colour, and mainly consist of magenta and phosphine. They dye a yellowish to brownish-red.

Cardinal, Amaranth, Geranium, and Russian Red are similar mixtures of inferior quality.

Maroon (Chestnut-Brown, Bordeaux for cotton, Crimson), which is also obtained from the mother liquors of magenta, consists chiefly of chrysaniline, mauvaniline, violaniline, phosphine, and rosaniline. It is met with in commerce as a powder or paste or in lumps. If not readily soluble in water it may be dissolved with the aid of a little hydrochloric acid. In alcohol it is freely soluble.

Maroon dyes from red-brown to dark claret shades and is applied in the same way as magenta. Silk is dyed in boiled-off liquor.

NEW MAGENTA (M.L.B.). $C_{22}H_{24}N_3Cl$.

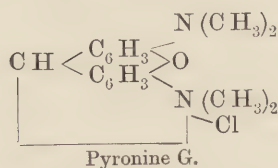
This new product is obtained by the condensation of diamido-ditolylmethane and orthotoluidine. It is the salt of a trimethyl-pararosaniline, and is analogously constituted to magenta, which it resembles in character and dyeing properties. New magenta forms a green powder, which is soluble in water with a bluish-red colour. The solution is turned yellow by excess of hydrochloric acid, but becomes red again on diluting with water. Caustic soda decolorises the solution, and produces a dirty red precipitate of the base. The dyestuff dissolves in concentrated sulphuric acid with a yellowish-brown colour; the solution becomes yellowish-brown to red on diluting, according to the quantity of water that is added.

Application.—New magenta is employed like ordinary magenta on the various textile fibres; the shade is more brilliant.

RHODAMINE.

The rhodamines (although basic dyestuffs) are closely related to the eosins; they will be fully treated in a special chapter, together with those colours. They yield dull shades on tanned cotton, and hence are little used on this fibre, but they are of great importance for the dyeing of wool and silk.

PYRONINE G, $C_{17}H_{19}N_2OCl$. PYRONINE B, $C_{19}H_{23}N_2OCl$.
(Leonhardt.)



Pyronine G and B are new basic dyestuffs obtained by the oxidation of tetramethyl- or tetraethyldiamidophenylmethaneoxide. The last-named compounds are prepared by the condensation of formaldehyde with dimethylmetamidophenol or diethylmetamidophenol respectively.

Pyronine dyes a brilliant very bluish-red similar to safflower-pink.

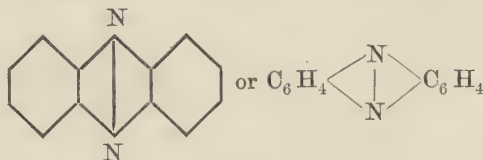
Cotton is mordanted with tannin and antimony, and dyed with $\frac{1}{2}$ to 2 per cent. of pyronine, in the same way as magenta. The shade is distinguished by unusual fastness to soaping.

For **wool** these dyestuffs are not suitable.

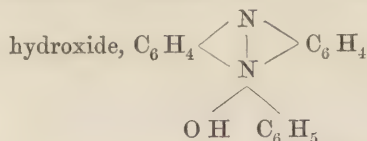
Silk is dyed with pyronine in neutral soap-baths, in the same way as magenta.

EURHODINES AND SAFRANINES.

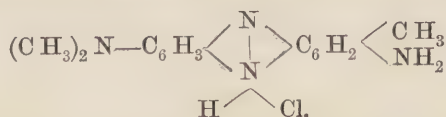
These colours are derivatives of phenazine, $C_{12}H_8N_2$:



The eurhodines are amidocompounds of phenazine, whereas the safranines are derivatives of the quaternary base, phenylphenazonium



NEUTRAL RED (Cassella) (TOLUYLENE-RED), $C_{15}H_{16}N_4 \cdot HCl =$



Neutral red is the hydrochloride of dimethyldiamidotoluphenazine, obtained by the action of nitrosodimethylaniline hydrochloride on metatoluylenediamine. The base of the dyestuff forms salts, with one, two, or three equivalents of acids; the monacid salts only are stable in aqueous solutions.

Neutral red forms an olive-black powder, which is readily soluble in water with a claret-red colour; the alcoholic solution is magenta-red with a brown-red fluorescence. The aqueous solution is turned from violet to blue by hydrochloric acid, while caustic soda produces a brownish precipitate. The solution of neutral red in sulphuric acid is green, and becomes, on diluting with water, at first blue and gradually purplish-red.

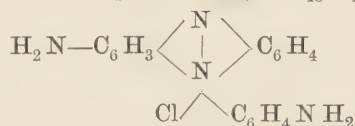
Cotton is mordanted with tannin and antimony and dyed with neutral red in a fresh neutral bath; the material is entered at the ordinary temperature and the bath heated slowly to 50°.

Neutral red yields a dull bluish-red shade, which is not fast to light.

Wool and silk are not dyed with neutral red.

SAFRANINE.

Various brands of safranines are manufactured, which consist of the mixtures of the hydrochlorides of various isomeric and homologous bases. The simplest representative of these is *para-amidophenyl para-amidophenazonium chloride* or *phenosafranine*, $C_{18}H_{15}N_4Cl$

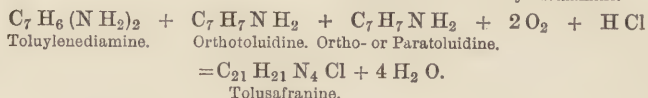
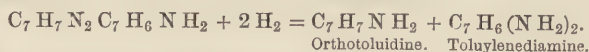


The safranines form salts with one, two, or three equivalents of acids; the monacid salts only are stable in solutions. By caustic soda the dyestuffs are precipitated, but the base is not separated in the free state thereby. Reducing agents form colourless *leucosafranines*, from which the dyestuffs are regenerated on oxidation by the air. The safranines dissolve in sulphuric acid with a green colour; the solution becomes first blue, then violet, and finally red on diluting with water (general reaction of the safranines).

Safranine B extra or **Phenosafranine** is obtained by the oxidation of a mixture of one equivalent of paraphenylenediamine and two equivalents of aniline.

It forms green glittering crystals, which dissolve in water with a red colour. The dyestuff resembles ordinary safranine in properties and application, except that the shade is more bluish.

Safranine T or **Ordinary Safranine** (*Pink*; *Safranine extra G*; *Safranine S*; *Safranine E*).—This dyestuff consists of a mixture of pheno- and tolosafranines. For its production aniline-oil (such as contains chiefly orthotoluidine) is converted with sodium nitrite and hydrochloric acid into amidoazo-compounds; the product is reduced with zinc and hydrochloric acid, and a mixture is obtained of toluylenediamine, orthotoluidine, and various homologous bases, certain quantities of ortho- or paratoluidine or aniline are added, and the mixture is subjected to oxidation by means of potassium bichromate. The following equations may explain the process:—



According to the composition of the materials—whether they contain more or less aniline or the one or other toluidine—the composition of the product varies slightly, and the shade becomes more bluish or more yellowish; the differences, however, are small, and the properties generally remain the same.

Ordinary safranine is generally a red-brown powder, which is readily soluble in water and in alcohol with a red colour; the aqueous, and especially the alcoholic, solution shows a fine yellow fluorescence. Hydrochloric acid turns the aqueous solution blue-violet and caustic soda causes a brown-red precipitate. With sulphuric acid the general reaction of the safranines (green solution, &c., p. 464) is obtained.

Safranine-Scarlet, Cotton-Scarlet, &c., are mixtures of safranine with other dyestuffs, such as auramine or chrysoidine; their solutions should not be heated beyond 80°, since auramine is decomposed by high temperatures.

Safranine-base is insoluble in ether, whereas auramine-base is soluble in this liquid; mixtures of safranine and auramine may be detected, therefore, with the aid of ether.

Application of the Safranines—Cotton.—The best results in dyeing cotton with the various safranines are obtained by previously mordanting with tannin and antimony and dyeing in a fresh bath; enter cold and heat slowly, not beyond 50°; add the dyestuff by degrees; a little acetic acid in the dye-bath makes the colours brighter. The shades are very fast to soaping, but rather fugitive to light. Stannic chloride, basic alum, or lead acetate can be used instead of antimony for fixing the tannin; but the shades thus obtained are inferior in fastness and purity. Very light shades can be dyed in a soap-bath without previous mordanting; but they are not at all fast to washing or to light. Safranine is sometimes used to shade alizarin-reds. It also occurs as an admixture to several commercial brands of benzopurpurin, but it can hardly be said to improve this colour when dyed as usual in a boiling bath.

Safranine is not very valuable for the dyeing of wool or silk.

Wool can be dyed with safranine in a neutral, acid, or alkaline bath; the colour is not fast to light, fading considerably within 24 hours. The dyestuff is sometimes added to reduced indigo to produce redder shades in the vat.

Silk is dyed in a bath of neutral soap. Prepare the bath with the dyestuff, enter the silk at 20° to 25° C. and heat to 50° or 60°; turn

until the desired shade is obtained ; wash and brighten in tartaric or acetic acid and dry. Brightening with sulphuric acid makes the shade bluer.

GIROFLÉ or METHYLENE-VIOLET (Durand). $C_{24}H_{27}N_4Cl$.

Giroflé is a safranine produced by the action of nitrosodimethylaniline on a mixture of metaxyloidine and paraxyloidine. The commercial product forms a brown paste or a greyish-green powder, not very soluble in water, but freely soluble in alcohol with a magenta-red colour. The aqueous solution is turned blue on addition of hydrochloric acid, if concentrated. Caustic soda gives a dirty red precipitate. Sulphuric acid dissolves the dyestuff with a green colour, which becomes first blue and then red on dilution with water. Giroflé is a useful dyestuff both for dyeing and printing cotton, and is applied exactly like the safranines. It dyes a red-violet shade and is principally used for toning alizarin-red. It is moderately fast to light.

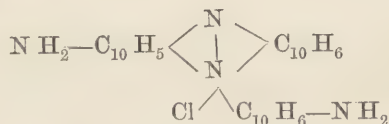
Methylene-violet (M.L.B.) is similar to or identical with giroflé.

ROSOLANE (M.L.B.)

This new dyestuff belongs to the class of the safranines. It is produced by oxidising a mixture of one equivalent of paramidodiphenylamine and two equivalents of orthotoluidine.

Rosolane yields a red-violet colour on silk, which is distinguished by superior fastness to light and to washing. It is also used for white dyeing of silk.

MAGDALA-RED, NAPHTHALENE-RED or NAPHTHYLAMINE-PINK. $C_{30}H_{21}N_4Cl =$



This dyestuff is the safranine of the naphthalene series and is constituted analogously to phenosafranine. It is prepared similarly to the ordinary safranine by reducing amidoazonaphthalene (from alphanaphthylamine) and oxidising the product after one equivalent of alphanaphthylamine has been added.

Magdala-red is a dark brown powder, not soluble in cold and sparingly soluble in hot water. It dissolves freely in alcohol with a cherry-red colour and a strong cinnabar-red fluorescence; by this property it is best recognised, as only some derivatives of resorcin, such as diazoresorufin, resemble it in this respect; the latter differ, however, from it in their behaviour towards caustic alkalis. Hydrochloric acid makes the solution of Magdala-red more bluish; caustic soda causes a red-violet precipitate. The solution in sulphuric acid is greyish-blue and turns bluish-red on dilution with water. Magdala-

red on reduction is converted into a leuco-compound from which the dyestuff is regenerated on oxidation by the air.

Application.—Magdala-red, on account of its high price, is used in small quantities only, and exclusively in silk dyeing. It yields a beautiful pink with a strong fluorescence, which is especially fine on velvet. It loses the brilliancy in deep shades and these are produced better and cheaper with other colours—*e.g.*, the eosins and rhodamines.

One part of dyestuff produces a light pink on 1000 parts of silk. Dye in a bath with neutral soap or boiled-off liquor; enter cold, and raise to 50° or 60°; brighten with acetic acid.

Magdala-red is faster than most of the basic colours to light, acids, and alkalies.

CHRYSOÏDINE. $C_{12}H_{12}N_4 \cdot HCl = C_6H_5N_2C_6H_3(NH_2)_2HCl$.

Chrysoïdine or *diamidoazobenzene chloride* is formed by the action of diazobenzene chloride on metaphenylene diamine. *Chrysoïdine R*, a homologous dyestuff, is produced from diazotoluene and toluylene diamine. *Cardinal-red* and *magenta-scarlet* are mixtures of magenta and chrysoïdine; under the names of *cotton-scarlet* or *cotton-ponceau* mixtures of safranine and chrysoïdine are sold.

The base of chrysoïdine ($C_{12}H_{12}N_4$) forms salts with one and with two equivalents of acids; the monacid salts only are stable in aqueous solutions. Chrysoïdine, being an azo-compound, is decolorised by reducing agents, but is not regenerated under any circumstances by oxidation—in which respect it differs from the other basic dyestuffs (except Bismarck-brown).

Chrysoïdine is sold in the form of a red-brown crystalline powder or black crystals having a green metallic reflex. It dissolves freely in water with an orange colour. Hydrochloric acid produces in the aqueous solution an orange-coloured and soluble gelatinous precipitate; caustic soda forms a yellow precipitate. Sulphuric acid dissolves it with a brownish-yellow colour; the solution becomes orange on dilution with water.

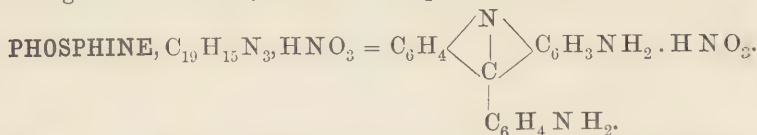
Application.—Chrysoïdine is not used much on silk and still less on wool; it is not suitable for printing, since it does not stand the influence of steaming. Mixtures of chrysoïdine with safranine are more permanent to light than those with magenta. Chrysoïdine is best dissolved in non-calcareous water at a temperature of 80°. The solution must not be kept for a long time, since it decomposes spontaneously.

Cotton can be dyed with chrysoïdine in light shades without any mordanting and without any additions to the dye-bath. For deep shades mordanting with tannin is required. The tannin can be fixed with antimony or basic alum; but no faster colours are obtained, and the less expensive mordanting with tannin alone is recommended. The mordanted cotton is dyed in a tepid bath, wrung out, and dried

without washing; a pure red-orange shade is obtained, which is not fast to light or to washing.

Wool is dyed with chrysoidine either in a neutral bath or in one containing 2 per cent. of alum or of bisulphate of soda; enter at 90°, work the goods for 15 minutes, allow to cool to 50° or 60°, wash in water which has been slightly acidulated with sulphuric acid, wring and dry. The shade is not fast.

Silk.—Dye in a weak soap-bath for half an hour at 50° to 60°, wash and brighten with acetic, tartaric, or sulphuric acid, wring and dry.



Chrysaniline, Aniline-Orange, Leather-Yellow, Philadelphia-Yellow, &c.

Commercial phosphine is not a uniform substance; it is a mixture of the nitrates of *diamidophenylacridine* and of homologous bases. *Diamidophenylacridine* ($C_{19}H_{15}N_3$) is also called *parachrysaniline*; the next homologous base *chrysaniline* ($C_{20}H_{17}N_3$) is also present in commercial phosphine. (See also *Impure magentas*.)

Phosphine is produced from the resinous bye-products and mother liquors of magenta obtained by the arsenic acid process. It comes into commerce as the nitrate (or hydrochloride), which forms a yellow or orange powder, readily soluble in water with an orange-yellow colour and a yellow-green fluorescence. The aqueous solution is not altered by hydrochloric acid; caustic soda produces therein a yellow flocculent precipitate. Sulphuric acid dissolves phosphine with a light yellow colour and a green fluorescence; the solution becomes deeper yellow on dilution with water.

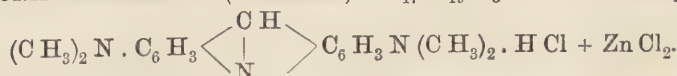
Application.—Phosphine is dyed exactly in the same way as magenta and safranine. It is a very costly dyestuff, and has been replaced of late to a great extent by chrysamin, toluylene-orange, and other products. In leather dyeing it is still used extensively. The commercial articles differ greatly in quality.

Cotton is dyed either unmordanted, or on tannin mordant which has been fixed with antimony or aluminium; a Nankin-yellow shade is obtained, which possesses considerable fastness to soap, but not to light.

Wool may be dyed with phosphine in a hot bath which is slightly acidulated with acetic acid. The dyestuff, however, is hardly used on wool, except in printing.

Silk is dyed with phosphine exactly as with safranine. A mixture of magenta and phosphine gives a fine scarlet on silk.

ACRIDINE-ORANGE (Leonhardt). $C_{17}H_{19}N_3 \cdot HCl + ZnCl_2 =$



Acridine-orange is the double salt of zinc chloride and the hydrochloride of *tetramethyldiamidoacridine*; the leuco-compound is produced by heating tetramethyltetraamidodiphenylmethane with acids and is subsequently converted into the colour-base by oxidation. Acridine-orange is a new basic dyestuff, which resembles phosphine. It is sold as an orange-coloured powder which dissolves in water and in alcohol with an orange colour and a greenish fluorescence. The aqueous solution is turned red on addition of hydrochloric acid, and gives a yellow precipitate with caustic soda. The solution in concentrated sulphuric acid is almost colourless with a greenish fluorescence, and becomes at first red and then orange on dilution with water.

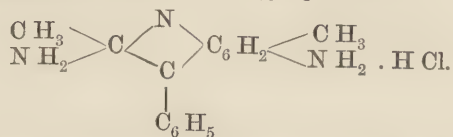
Application.—Acridine-orange gives orange shades, which are very fast to soaping. It is recommended for the dyeing of leather, which material acquires a peculiar golden lustre thereby.

Cotton is mordanted, as usual, with tannin and antimony, and dyed with the addition of 2 grms. (3 oz.) of alum per litre (10 galls.) of the dye-liquor. The colour gives good results in dyeing and printing.

Wool is dyed without a mordant.

Silk is dyed in a soap-bath broken with acetic acid; the shade shows a fine greenish fluorescence.

BENZOFLAVINE (Oehler). $C_{21}H_{19}N_3 \cdot HCl =$



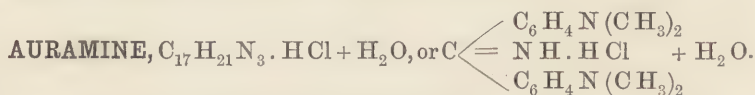
Benzoflavine is *diamidodimethylphenylacridine*; it is produced by condensing benzaldehyde with two equivalents of metatoluylenediamine and oxidising the intermediary product, hydrodiamidodimethylphenylacridine (the leuco-compound), with ferric chloride.

Benzoflavine is sold as a brownish-orange coloured powder, which dissolves sparingly in cold water, better in hot water, with a yellow colour and a yellowish-green fluorescence. The alcoholic solution is reddish-yellow and shows a green fluorescence. The aqueous solution gives an orange precipitate on addition of hydrochloric acid and a yellowish-white precipitate with caustic soda. Sulphuric acid dissolves the product with a greenish-yellow colour and a very strong green fluorescence; on dilution with water, at first, a yellowish solution and, then, an orange precipitate is formed.

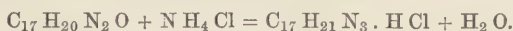
Application.—Benzoflavine is applied in the same way as the other basic dyestuffs; it is not of much importance in wool and silk dyeing. Dissolve by stirring 1 part of dyestuff in 100 parts of boiling water to which 3 parts acetic acid have been added; boil for 15 minutes. Add the solution to the dye-bath through a fine hair-sieve. Cold solutions must be heated up and filtered before use.

Cotton may be dyed with or without mordanting. Enter the cotton, which has been mordanted with tannin and antimony, into the luke-warm bath, and heat to 80°; the temperature may, however, be raised to boiling without injury to the colour. A pure yellow shade is obtained, which is fairly fast to soap and light.

Benzoflavine is especially well adapted for shading malachite-green and brilliant green; it gives a fine scarlet with safranine. Benzoflavine is especially valuable in calico-printing, since it is not so sensitive to high temperatures, acids, and chlorine, as auramine.



Auramine or *imidotetramethyldiamidodiphenylmethane hydrochloride* is produced by condensing tetramethyldiamidobenzophenone and ammonium chloride with the aid of zinc chloride:



Auramine is offered to the trade in pure quality as auramine O; in addition some brands, containing more or less dextrin, are found in the market under the names auramine I., II., or III.

Auramine forms a yellow powder, which is sparingly soluble with a light yellow colour in cold, but freely soluble in hot water, or acidulated water. The aqueous solution is decomposed on boiling into the constituents from which auramine is prepared, which decomposition takes place more rapidly in acid than in neutral solutions. The aqueous solution becomes darker on addition of hydrochloric acid and gives a white precipitate with caustic soda. The solution in sulphuric acid is colourless and is turned a light yellow on dilution with water.

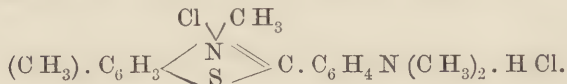
Application.—Auramine is valuable for shading other basic colours, such as magenta, safranine, and the greens. It should be dissolved in hot water, which, however, must not be heated over 80°, neither must the temperature of the dye-bath be raised above this point. If it should be necessary to acidify the bath, acetic acid must be used, not mineral acids.

Cotton is mordanted in the usual manner with tannin and antimony; for light shades the use of small quantities of mordanting materials is advisable when it is desired to obtain a pure yellow—*i.e.*, one which is not reddish in tone. The mordanted cotton should be worked for 20 to 30 minutes in a weak soap-bath ($1\frac{1}{2}$ gr. ($2\frac{1}{2}$ oz.) neutral soap per litre (10 galls.)) and then rinsed thoroughly in water before it is dyed. Dye in a fresh luke-warm bath, wring and dry at the usual drying temperatures; if necessary, the dye-bath may be heated to 80°, but not higher. In printing, the colour must not be steamed under pressure. Auramine on tannin and antimony is fairly fast to soap and to light, but very sensitive to chlorine. When dyed alone it gives a pure yellow; it possesses importance in cotton dyeing for the production of compound shades.

Wool is dyed in a neutral bath for half an hour at 60° to 70°. Auramine, however, is not well adapted for wool dyeing, since it is too easily decomposed in hot solutions in the presence of acids.

Silk is dyed in a neutral bath or with a little neutral soap at 60° to 70°. The colour must be added gradually and the silk be turned very quickly. After dyeing and rinsing the goods are brightened with a small amount only of acetic acid, on account of the sensitiveness of auramine to acids. Silk is rarely dyed with auramine.

THIOFLAVINE T (Cassella). $C_{17}H_{19}N_2S \cdot Cl \cdot HCl =$



Thioflavine T is a new basic dyestuff which is related by its chemical constitution to thioflavin S, a yellow direct cotton colour. Thioflavine T is the hydrochloride of *dimethyldehydrothiotoluidinemethyl chloride* and is produced by heating dehydrothiotoluidine with methyl alcohol and hydrochloric acid in closed vessels to 170° C.

Thioflavine T is an orange-yellow powder, which dissolves in water and in alcohol with a yellow colour; the alcoholic solution shows a greenish fluorescence. Hydrochloric acid does not alter the appearance of the aqueous solution; caustic soda produces a yellow precipitate. The solution in sulphuric acid is colourless and shows a dark green fluorescence; on dilution with water a light yellow solution is obtained.

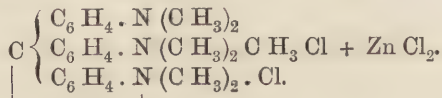
Application.—Thioflavine T yields pure greenish-yellow shades, and is a very useful dyestuff for the various fibres. It is employed with advantage for shading other basic colours, since it is not sensitive to high temperatures and resists well the action of acids and chlorine. It is exceedingly fast to light.

Cotton is mordanted with tannin and antimony, and dyed at 75° with $\frac{1}{2}$ per cent. to 2 per cent. of hydrochloric acid (of the weight of dyestuff). The temperature may be raised to boiling. The colour is fairly fast to soap and extraordinarily fast to light.

Wool is dyed in a boiling bath with the addition of 10 per cent. of Glaubersalt, and 10 per cent. of sodium bisulphite to the bath. Thioflavine T used in small quantities ($\frac{1}{20}$ per cent.) yields beautiful pure greenish-yellow shades on wool. If required, thioflavine T may be dyed for shading purposes without bisulphite.

Silk is dyed in a boiling soap-bath and brightened with sulphuric acid. The shade possesses a green fluorescence.

METHYL-GREEN. $C_{26}H_{33}N_3Cl_2 + ZnCl_2 =$



Light-Green. Vert Etincelle. Vert de Methylaniline.

This product is a chloromethylated methyl-violet and is manufactured by the action of methyl chloride on methyl-violet. A more bluish-green dyestuff is prepared by using ethyl bromide instead of methyl chloride.

By the action of methyl or ethyl chloride, bromide or iodide, &c., on rosaniline and on Hofmann's violet similar green colouring matters were formerly produced—*e.g.*, *iodine-green*, *bright green*, or *vert lumière*. These were the first green aniline colours prepared; they have long disappeared from the market, having been replaced, first by the cheaper methyl-green and, later, by the benzaldehyde-greens.

Methyl-green is sold either in small green crystals with a golden lustre or as a light green powder. It dissolves readily, with a bluish-green colour, in water and in alcohol, but not in amyl alcohol (distinction from benzaldehyde-green). The aqueous solution is turned reddish-yellow by hydrochloric acid, an unstable triacid salt being formed; hence the colour becomes yellowish-green on dilution with water. Caustic soda decolorises the aqueous solution, liberating the soluble colour base in the free state. Methyl-green dissolves with a reddish-yellow colour in sulphuric acid; the solution becomes green on dilution with water. When heated over 100° C., methyl-green is decomposed into methyl-violet and methyl chloride.

Solutions of methyl-green yield, on addition of picric acid, a dark green crystalline precipitate, which is nearly insoluble in water, but readily soluble in alcohol; it was sold for a time as *spirit-soluble green*.

Methyl-green should be entirely soluble in water with a bluish-green colour.

Application.—Methyl-green is still used to some extent on silk, because it can be shaded better than the other green dyestuffs with picric acid. For the dyeing of cotton and wool it has been replaced by benzaldehyde-green, brilliant green, acid-green, &c., since these dyestuffs require no mordant on wool, are not altered by heat, and are better suited for compound shades. Methyl-green, however, does not rub so much as malachite-green. In dyeing with methyl-green the bath should never be heated to the boiling point, copper vessels must be avoided, and calcareous water should be slightly acidulated.

Cotton is mordanted with tannin and antimony and dyed in a bath the temperature of which may be raised to 50°. First, two-thirds of the required amount of dyestuff are added and the rest after 20 minutes dyeing. After washing, the goods are brightened in a weak acid bath. The shade is not fast to light.

Wool must be mordanted before dyeing with sodium hyposulphite (thiosulphate). Both in mordanting and in dyeing, the wool must not come in contact with metals, such as copper, lead, or iron, that are liable to give rise to stains of metallic sulphides. Pipes which are coated with tin can be used for heating the dye-bath.

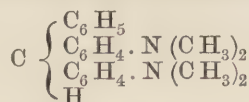
Dissolve for 100 kgs. (lbs.) wool, 20 kgs. (lbs.) of hyposulphite and 10 kgs. (lbs.) of alum; when all is dissolved add 4 kgs. (lbs.) of sulphuric acid. Enter the wool into the milky liquid at 40° and turn it for about 1 hour while the temperature is raised to 80° but not higher. Then wash the wool thoroughly in water, and pass it, after washing, through a bath containing a very small amount of ammonia. The ammonia bath may be dispensed with if 2 to 4 per cent. of borax or of acetate of soda are added to the dye-bath. Dye in a neutral bath or in one slightly acidulated with acetic acid at a temperature not exceeding 80°; wash and dry. If a yellower shade is desired wool can be dyed with a mixture of methyl-green and picric acid; but the dye-bath must be prepared in a peculiar way, since picric acid dyes in acid baths only: for 100 litres (100 galls.) of liquor 100 grms. (1 lb.) of acetate of zinc is added; this will combine with the sulphur deposited in the fibre by mordanting, and form the sulphide of zinc, which serves as a mordant just as well as the sulphur itself; while acetic acid is set at liberty in sufficient quantity to acidify the bath. If picric acid only should be fixed by the fibre—from over-acidity of the bath—some sodium acetate is added; the amount necessary will not exceed three times the weight of the zinc salt employed.

Silk is dyed in a lukewarm soap-bath, slightly acidulated with sulphuric or acetic acid. The temperature may be raised to 50°. After dyeing, the silk is washed and brightened with acetic or tartaric acid. If a yellower shade is desired picric acid is added to the *brightening* bath, and the goods are dried at once and without rinsing, so as not to remove any picric acid.

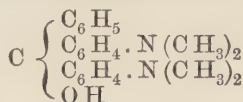
MALACHITE-GREEN. $C_{23}H_{25}N_2Cl$, &c. (see below).

Benzal-Green, Benzoyl-Green, Victoria-Green; Imperial, New, Fast or Diamond-Green.

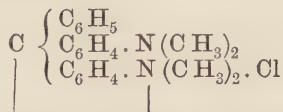
Malachite-green is a derivative of diamidotriphenylmethane. It is obtained by first condensing benzaldehyde with dimethylaniline to form tetramethyldiamidotriphenylmethane or leuco-malachite-green; and, subsequently, oxidising this product into malachite-green:—



Leuco-base of malachite-green.



Base of malachite-green.



Chloride of malachite-green base.

Malachite-green is sold in the form of several salts and double salts. The colour-base has the composition $C_{23}H_{26}N_2O$, and loses one equivalent

lent of water in forming salts as shown by the above graphic formula. It forms salts with one and with two equivalents of acids; the monacid salts only are stable compounds in aqueous solutions. The following two salts are commercial products known as malachite-green, &c. :—

1. *Oxalate*, $(C_{23}H_{25}N_2)_2C_2O_4 + 2H_2C_2O_4$; tablets with a metallic-green lustre.

2. *Zinc double chloride*, $3C_{23}H_{25}N_2Cl + 2ZnCl_2 + 2H_2O$, occurs either as prismatic crystals with a yellow-beetle-green lustre or as a greenish powder.

These two salts are called without distinction by the same names in the trade.

An inferior quality is sometimes sold, which consists of the hydrochloride combined with ferric chloride. The picrate, which is insoluble in water, is sold as *malachite-green soluble in spirit*.

Liquid malachite-green is the hydrochloride in aqueous solution; it is prepared from the mother liquors from the crystallisation of the oxalate, and contains about 20 per cent. of pure green. Malachite-green dissolved in acetic acid is also met with in the trade under the name of *liquid malachite-green*.

Malachite-green B and 4 B are mixtures with methyl-violet.

Malachite-green is soluble in water, in alcohol, and in amyl alcohol (thus differing from methyl-green), with a bluish-green colour. The aqueous solution becomes reddish-yellow on addition of hydrochloric acid; the original colour is restored on dilution with much water. Caustic soda produces in the aqueous solution a pale yellowish-green precipitate. Sulphuric acid dissolves the dyestuff with a yellow colour; on dilution with water the solution becomes at first orange and then olive-green to bluish-green. Malachite-green yields a leuco-product by reduction; the dyestuff is regenerated under the influence of strong oxidising agents, but not by the action of atmospheric oxygen.

Application.—Malachite-green serves for the dyeing and printing of all fibres. Both forms, the oxalate and the double zinc salt, are used in precisely the same manner; in calico-printing, however, the oxalate is preferred, because zinc chloride weakens the vegetable fibre on steaming. The dyestuff is dissolved in hot water and filtered; calcareous water is corrected with acetic acid, for wool dyeing, with bisulphate of soda. Solutions of malachite-green should not come in contact with copper.

In dyeing with malachite-green the liquor can be heated to boiling without any risk (if auramine has been added for shading purposes, the temperature, of course, must not be too high). The dye-bath is not exhausted. Malachite-green yields beautiful green shades, which are not fast to light, soaping, or milling.

Cotton is dyed, similarly with the other basic dyestuffs, after previous mordanting with tannin and antimony. Work the cotton for

half an hour in a warm bath, which may be slightly acidulated with acetic acid, add the colour solution gradually, wring out, and dry without washing. By raising the temperature to the boil the shade loses in depth, but becomes brighter and faster to soaping; greater fastness to soaping is also obtained by drying the mordanted cotton before dyeing. A very light soaping of the dyed material brightens the shade. Tannin and basic alum, or basic alum alone, may be used for mordanting, or, for bright shades, Turkey-red oil and alum; the tannin-antimony method, however, is the best also for this dyestuff. Dark shades are produced with tannin and iron:—(1) Mordant with pyrolignite of iron (4° Tw.), oxidise by ageing, pass through weak lime water, wash, pass through solution of tannin, and dye as before; if the shade comes out too full it can be made lighter by passing the goods through a weak bath of stannous chloride. (2) Mordant first with tannin, and, subsequently, with pyrolignite of iron (6° Tw.), and dye as before. (3) Pad the material in a bath containing 1 part of tannin and 3 parts (by weight) of pyrolignite of iron (15° Tw.) in 100 parts of water; dry in the hot flue and dye as before.

Malachite-green may be mixed, in cotton dyeing, with any of the basic colours. The direct cotton colours are very well adapted for shading this dyestuff and their use may save the mordanting operation. To obtain, for example, a yellower tone, dye first with chrysamin and top in a cold bath with malachite-green; heating of the dye liquor destroys the colour-lake of the direct dyestuff with malachite green. A yellowish-green can also be produced by mordanting with alum; fixing with phosphate of soda; and dyeing, first, in quercitron-extract and, then, in malachite-green.

Wool is dyed with malachite-green either without a mordant or after previous mordanting with sodium thiosulphate.

(1) *Dyeing without a Mordant.*—The wool is dyed in a bath slightly acidified either with an acid (sulphuric, acetic, &c.) or with bisulphate of soda or sulphate of alumina. If the bath is not acid, it is imperfectly exhausted, and if the water is calcareous the exhaustion is even less complete. On the other hand, an excess of acid also prevents the bath from being exhausted; hence the bath should only just give an acid reaction. An addition of 20 per cent. of Glaubersalt, or 8 per cent. of magnesium sulphate, or 6 per cent. of zinc sulphate, or 3 per cent. of alum (of the weight of the wool) tends to diminish the effect of excessive acidity. The wool is dyed at the boil for half an hour, washed, and dried.

(2) *Dyeing of Mordanted Wool.*—The wool is mordanted exactly as described for methyl-green. This process is longer, and the wool acquires a peculiar appearance and smell; but it is necessary for the production of deep shades, while the colour becomes faster to light and milling and rubs less. The wool is dyed at the boil without any additions, washed and dried. A small quantity of basic alum in the

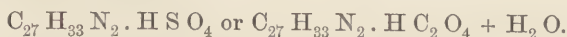
dye-bath prevents felting of the wool and gives greater fastness to milling. The addition of soap to the dye-bath cannot be recommended in either case, because of the formation of a sticky zinc soap if the double salt of zinc be used.

The basic or the acid colours may be used in the same bath with malachite-green, for shading purposes, both on wool and silk.

Silk is dyed in boiled-off liquor to which sulphuric acid has been added until the bath is only slightly alkaline. Heat the bath to 70° or 80°, add the colour solution and work the goods for half an hour, wash, brighten with a little acetic acid, and dry.

As to shading, see the remark just made under *wool*. If malachite-green is shaded with picric acid, the goods should be dyed, first, with the green and, then, topped with picric acid.

BRILLIANT GREEN.



New Victoria-Green, Ethyl-Green, Fast Green J., Emerald-Green.

Brilliant green is homologous with malachite-green, and is obtained when, in the manufacture, diethylaniline is substituted for dimethylaniline. The properties and modes of application are the same for both dyestuffs.

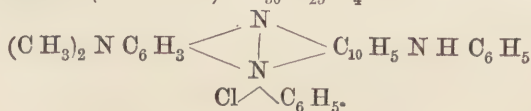
Brilliant green comes into commerce as the sulphate, which forms small crystals having a golden lustre; or as the oxalate, which crystallises in large prisms. The reactions are those of malachite-green; the solution is less bluish.

Brilliant green dyes a yellower and more brilliant shade than malachite-green, but possesses less colouring power.

VICTORIA-GREEN 3 B or NEW FAST GREEN 3 B. $\text{C}_{23}\text{H}_{23}\text{N}_2\text{Cl}_3$.

This dyestuff is a chlorinated malachite-green, and is produced in a similar way from dichlorbenzaldehyde and dimethylaniline. It forms a green crystalline powder with a metallic lustre, which is little soluble in cold, more freely in hot water, and dissolves readily in alcohol with a greenish-blue colour. The hot aqueous solution becomes gelatinous on cooling. Hydrochloric acid makes the solution yellow; addition of much water makes it green again; caustic soda turns it reddish-yellow, producing some precipitate. The solution in sulphuric acid is yellow; dilution with water changes it to orange and to yellowish-green if the dilution is continued. Victoria-green 3 B is applied to the textile fibres in the same way as malachite-green. It dyes a more bluish shade.

AZINE-GREEN (Leonhardt). $\text{C}_{30}\text{H}_{25}\text{N}_4\text{Cl}$ =



Gentian-Blue 6 B, Opal-Blue, Night-Blue, &c.—Rosaniline-blue is a phenylated magenta, produced by heating rosaniline-base in the presence of benzoic acid with a large excess of pure aniline (aniline for blue) to 180°. Inferior qualities are obtained by using magenta and sodium acetate for rosaniline-base and benzoic acid respectively. Rosaniline-blue in the purest form is a salt of triphenylrosaniline containing varying amounts of triphenylpararosaniline salt, according to the composition of the magenta from which it was prepared. In each of the three amido-groups of rosaniline one atom of hydrogen (not both) can be replaced by *phenyl* and *mono-, di-, and triphenylrosaniline* be produced. Monophenylrosaniline dyes a red-violet, diphenylrosaniline a blue-violet, and triphenylrosaniline a pure sky-blue shade.

By reducing the quantity of aniline-oil the material is not completely phenylated, so as to contain mono- and diphenylrosaniline; such products yield more or less dull and reddish-blue colours. The reddish shade of the inferior blues is particularly noticeable in artificial light, whereas the colour of the highest qualities appears as beautiful in artificial light as in daylight; hence the latter are called *light-blue* or *night-blue* (*bleu lumière; bleu de nuit*).

The purest rosaniline-blue is brought into the market as the chloride, sulphate, or acetate, under the names of *blue, green shade, blue 6 B* and *5 B, base-blue, opal-blue, Gentian-blue 6 B, Hessian blue, Lyons-blue, light-blue, &c.*

The inferior (less phenylated) rosaniline-blues are sold as *blue 4 B, 3 B, 2 B, B, Gentian-blue, imperial blue, Humboldt-blue* and as *blue R, Parma-blue, or Dahlia*. Blue R possesses a decidedly reddish shade and may be considered as an intermediate compound between spirit-blue and spirit-violet.

Rosaniline-blue forms salts with one, two, or three equivalents of acids; the monacid salts only are stable. It yields a leuco-compound *triphenyl-leucaniline* on reduction, which is readily reconverted into the blue dyestuff by oxidising agents.

Commercial rosaniline-blue is a brown, greyish-green or violet-blue powder without a metallic lustre. It is not soluble in water and sparingly soluble in alcohol; the acetate is fairly soluble in alcohol and is sometimes sold in solution. The alcoholic solution of rosaniline-blue has a beautiful blue colour, and is turned more greenish-blue by hydrochloric acid, red-brown by caustic soda. Sulphuric acid dissolves the dyestuff with a brownish-yellow colour; on dilution with water a flocculent blue precipitate is obtained.

The value of rosaniline-blue depends chiefly on the beauty of the shade, which is estimated by a dye-trial.

Application.—The rosaniline-blues are not much used in cotton dyeing or printing, and to a limited extent only on wool (when fastness to milling is required); they are dyed on silk when a bright

and very pure blue is demanded, such as cannot be obtained with the soluble blues. The rosaniline-blues are now almost completely replaced by the Victoria-blues, which are faster to milling, but less fast to light.

The rosaniline-blues are dissolved in 40 to 50 times their weight of methylated spirits, and the solution is gradually added to the dye-bath.

Cotton is best prepared with soap and aluminium acetate as indicated on p. 454. The mordanted cotton is entered into a fresh luke-warm bath and the alcoholic solution of the colour is added very gradually, whilst the bath is slowly heated to the boil. After a good washing in water the process is completed by a final soaping in a weak soap-bath, to which so much acetic acid has been added as to make it slightly turbid.

Cotton can also be impregnated with soap only and then be dyed in a fresh bath, to which aluminium acetate has been added; or it may be mordanted with tannin and dyed in a fresh bath containing alum.

Wool.—Prepare the bath with 5 per cent. of alum, 2 per cent. of sulphuric acid, and 1 per cent. of stannic chloride (of the weight of the wool); for the green shades 10 to 12 per cent. of alum without sulphuric acid, for the red shades 4 to 8 per cent. of sulphuric acid without alum, may be used; an addition of large quantities of common salt or Glaubersalt to the bath, to raise the boiling point, is advantageous. Turn the wool in the dye-bath, first at 60°, then add the alcoholic colour-solution gradually and bring to the boil; dye about 30 minutes, wash and dry. Better results are obtained by first boiling the wool 1 hour with 5 per cent. of tartar, 1 per cent. of tin spirits, and 4 per cent. of alum, washing, and dyeing with addition of 2 per cent. of sulphuric acid.

Silk is dyed in a bath of boiled-off liquor which has been acidified with sulphuric acid; turn the silk in the luke-warm bath, then add the colour-solution gradually, and heat to the boil; wash and brighten with sulphuric acid.

Rosaniline-blues, soluble in spirit, appear redder on silk than on wool; the difference is very considerable in artificial light, when the shade on wool is a pure blue, whereas that on silk appears decidedly violet.

DIPHENYLAMINE - BLUE. $C_{37}H_{30}N_3.Cl$. Bavarian Blue.

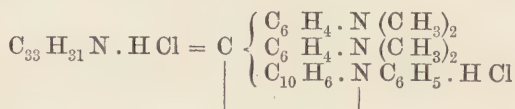
Diphenylamine-blue or *triphenylpararosaniline chloride* is produced by heating diphenylamine with oxalic acid to 130°. It forms a brown powder insoluble in water and sparingly soluble in alcohol with a beautiful blue colour. It dissolves in sulphuric acid with a brownish-yellow colour; the solution yields a blue precipitate on diluting with water.

Diphenylamine-blue is very little used on account of its high price; it is used in silk dyeing only. It gives a finer blue shade than rosaniline-blue or any other blue.

Methyl-blue and **ethyl-blue** are methylated and ethylated diphenylamine-blues.

Applications. (See *Rosaniline-blue*).

VICTORIA-BLUE B or **B S** (B. A. S. F., Bindschedler).



Victoria-blue B is the hydrochloride of *tetramethylphenyltriamidodiphenyl-naphthylcarbinol* and is produced by the action of phenylalphanaphthylamine on tetramethyldiamidobenzophenone chloride.

Victoria-blue B forms salts with one, two, or three equivalents of acid; only the monacid salts are stable. It yields a leuco-compound, and is regenerated therefrom by oxidising agents.

The commercial article forms a violet powder or a granular mass with a coppery reflex. It dissolves in warm water and in alcohol with a deep blue colour. The aqueous solution becomes turbid by continued boiling, the free colour-base being thrown down as a reddish resinous precipitate; acetic acid prevents this decomposition. In the presence of small quantities of mineral acids Victoria-blue does not dissolve as well as in pure water; large quantities, however, make it more soluble by forming diacid and triacid salts. Hydrochloric acid produces a blue precipitate in the aqueous solution, which redissolves on addition of more acid; the solution becomes at first green, then yellowish-brown, and contains the diacid and triacid salts. Caustic soda produces in the aqueous solution a red-brown precipitate. Sulphuric acid dissolves the dyestuff with a reddish-brown colour, which becomes yellow, olive-green, and blue on diluting with water.

Application.—Victoria-blue B is employed on all fibres, and dyes a very bright and pure blue, which is fairly fast to soaping and milling and mild alkalies, but not fast to light.

In dyeing with Victoria-blue calcareous water must be corrected with acetic acid. It is advisable to proceed as follows:—The dry colour is mixed to a paste with acetic acid—about 750 c.c. ($\frac{3}{4}$ pint) for 1 kg. (1 lb.) of dyestuff—and allowed to stand for some hours; hot water is then poured over the mixture, it is well stirred and the clear solution is filtered before use. The acetic acid has no injurious effect in dyeing.

Cotton is mordanted with tannin and antimony in the usual manner and subsequently worked in a warm soap-bath as described on p. 453. The soaping makes the ultimate shade purer and more even. Chromium mordant has been recommended for fixing the tannin, but it offers no advantages in dyeing; in calico-printing excellent results are obtained with chromium acetate (without tannin). Dye the mordanted cotton in a lukewarm bath, which contains for

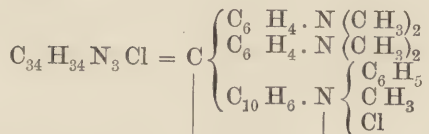
10 kgs. (10 lbs.) of cotton 650 c.c. ($\frac{2}{3}$ pint) of aluminium acetate (10° Tw.); add the colour gradually, work the cotton 30 to 45 minutes, wring and dry; the bath is kept moderately warm or hot, as required by the circumstances. Brighter though not fast shades are obtained with Turkey-red oil or soap and acetate of alumina.

Wool is dyed with acetic or other acids or acid salts; the shade becomes brighter by these additions, although less intense, and the dye-bath is not thoroughly exhausted. Boil the wool with 5 per cent. of aluminium sulphate and 5 per cent. of acetic acid 30 minutes, then add the colour solution to this bath, dye at the boil for 30 to 45 minutes, turning frequently, wash and dry.

Victoria-blue on wool is very liable to rub owing to the superficial fixation of an insoluble blue on the fibre. This may be remedied and the shade be brightened at the same time by a subsequent soaping. The boiling with aluminium sulphate before dyeing tends also to prevent the rubbing.

Silk is dyed with Victoria-blue in a bath of boiled-off liquor which has been acidulated with sulphuric acid. Add the colour solution to the warm bath, work the silk for 15 minutes, heat to the boil, and dye until the desired shade is obtained, wash, soap (if necessary), and brighten with acetic acid; dry.

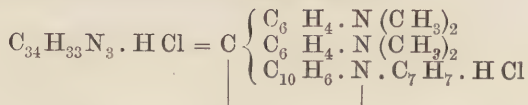
VICTORIA-BLUE 4 R (B. A. S. F., Bindschedler).—



This dyestuff is *pentamethylphenyltriamidodiphenylnaphthylcarbinol chloride*. It is manufactured in the same way as Victoria-blue B, by the action of methylphenylalphanaphthylamine on tetramethyldiamidobenzophenone chloride. Victoria-blue 4 R strongly resembles Victoria-blue B in its general character and tinctorial properties, except that it dyes a redder shade. It is sold as a violet powder with a bronze reflex and dissolves in water with a blue-violet colour.

Application. See *Victoria-blue B*.

NIGHT-BLUE (B. A. S. F., Bindschedler).—



Night-blue is the hydrochloride of *tetramethyltolyltriamidodiphenylnaphthylcarbinol*; it is obtained by a process similar to that used for the Victoria-blues (to which it is related) by the action of paratolylalphanaphthylamine on tetramethyldiamidobenzophenone chloride. It comes

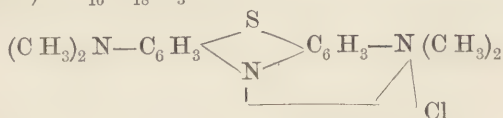
into the market as a violet powder with a bronze reflex, which dissolves in water with a blue colour; the solubility is increased by acetic acid.

Mineral acids precipitate the night-blue at first from the aqueous solution and then redissolve it with a brownish-yellow colour, diacid and triacid salts being formed. Caustic soda precipitates the colour-base as a red-brown precipitate, which is quite insoluble in water. The solution of night-blue in sulphuric acid is brown, and becomes olive-green and blue on addition of water.

Night-blue is completely precipitated from the aqueous, or slightly acid, solutions by picric acid, naphthol-yellow, and many other dyestuffs. A method has been founded on this fact to estimate such dyestuffs quantitatively. (See *Analysis*, Part XI.)

Application.—Night-blue dyes an extremely pure shade of blue, which is fast to soap on wool and silk. The colour on silk is of extraordinary beauty. In dyeing, special care must be observed in rectifying calcareous water. The dyeing processes are identical with those given for Victoria-blue B.

METHYLENE-BLUE or **ETHYLENE-BLUE** (B. A. S. F.; M. L. B.; Berlin; Oehler). $C_{16}H_{18}N_3S Cl =$



Methylene-blue belongs to the group of the *thiazines* or *thionine*-colours. It is a derivative of *thiodiphenylamine* or *thiazine*, and further of *thionine* or *paradiamidothiodiphenylamine*; the dyestuff is the chloride of *tetramethylthionine*. Methylene-blue is manufactured by various methods; the oldest process, which is still used, is the following:—Nitrosodimethylaniline is reduced by means of sulphuretted hydrogen and, subsequently, oxidised with ferric chloride in the presence of an excess of sulphuretted hydrogen. *Methylene-red*, a dyestuff of no practical value, is formed as a bye-product.

Methylene-blue forms monacid and diacid salts; the monacid salts only are stable compounds. Reducing agents convert methylene-blue into a leuco-compound from which the blue dyestuff is regenerated by oxidising agents. Methylene-blue occurs in commerce either as the hydrochloride or, usually, as the double salt with zinc chloride having the composition $2(C_{16}H_{18}N_3S Cl) + Zn Cl_2 + H_2 O$. The double salt forms a dark blue or brown powder with a bronze reflex and is readily soluble in water, less in alcohol, with a greenish-blue colour; the hydrochloride forms dark blue leaflets which are readily soluble in water and in alcohol with a greenish-blue colour. Hydrochloric acid does not alter the aqueous solution, caustic soda makes it more violet, and, when added in a concentrated state and in excess, produces

a dirty-violet precipitate. The solution in sulphuric acid is yellowish-green, and becomes blue on diluting.

Application.—Methylene-blue possesses little value for the dyeing of wool and silk, since for these fibres other blue dyestuffs of greater brilliancy and fastness can be used. On the other hand, it is of great importance for cotton dyeing, and especially calico-printing, on account of its relative fastness both to light and to soap. It replaces for many purposes vat-indigo and is often used to brighten indigo shades. Compound shades are produced by dyeing methylene-blue with methyl-violet (see *Marine-blue*), malachite-green, safranine, and other basic dyestuffs.

Cotton is mordanted in the usual manner with tannin and antimony, and subsequently soaped as described on p. 453. For very dark indigo shades the mordanted cotton is passed through a weak solution of pyrolignite of iron instead of being soaped; or a bath of pyrolignite of iron at 6° Tw. may be substituted for tartar emetic; after the treatment with iron liquor the cotton should be passed through weak lime water and finally well washed before dyeing. Very deep shades can also be produced by working the cotton first in catechu, passing it through an antimony solution and dyeing in methylene-blue. The dyeing takes place in each case in a fresh bath. Methylene-blue is liable to dye uneven and must be used with great care; the colour is added in small portions, the dye-bath should not be warmer than 20° to 25° C. at the beginning, and after some colour has been taken up it should be heated very gradually to 70° or 80° or higher, if required; a small amount of acetic acid in the dye-bath acts favourably for level dyeing. The shades obtained vary from a greenish-blue of not peculiar brightness—on antimony mordant—to deep indigo-blue—on iron mordant; a greater brilliancy can be imparted to them by an after treatment in a very weak bath of stannous chloride or sodium bisulphite.

Methylene-blue on cotton is distinguished by remarkable fastness to light and soap. It is much faster than most other basic colours; but in this respect does not compare with vat-indigo, though it possesses the advantage of not rubbing.

A pure blue without a greenish tone can be produced with methylene-blue by means of tannate of aluminium. Mordant the cotton with aluminium acetate, age, pass through a chalk bath, wash well, pass through a weak tannin bath and dye as before. The shade is fairly fast to soap.

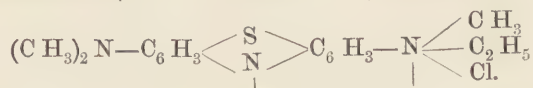
Wool is dyed with methylene-blue in an alkaline bath. Prepare the dye-bath with the colour-solution, and with 1 to 2 per cent. (of the weight of the wool) of soda crystals or ammonium carbonate or borax; or a small quantity of ammonia may be used; enter the wool and heat slowly to boiling, boil for 30 to 45 minutes, wash and dry.

Silk is dyed in a bath containing boiled-off liquor. Add the colour-

solution to the bath, enter the silk, heat to boiling and boil for 20 minutes; wash, brighten with acetic or tartaric acid, and dry.

Marine-Blues are mixtures of methylene-blue and methyl-violet. They are used in the same way as methylene-blue.

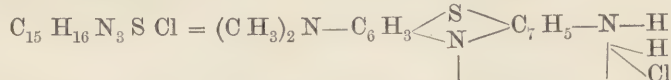
THIONINE-BLUE (M. L. B., Berlin). $C_{17}H_{20}N_3S\text{Cl} =$



This is a new dyestuff which bears a close relation to methylene-blue, being *trimethylethylthionine chloride*. For its production paramidodimethylaniline is oxidised in the presence of sodium thiosulphate and the product of this reaction is oxidised in the presence of ethylmethylaniline. This second intermediary product is converted into the leuco-compound of thionine-blue by boiling with chloride of zinc, and from the leuco-compound the dyestuff is obtained by oxidation.

Thionine-blue resembles methylene-blue extremely in its general character and tinctorial properties. It is also sold in the form of the zinc double salt. The solubility and reactions are like those of methylene-blue, as also the processes of dyeing.

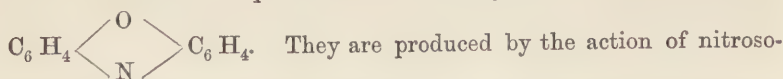
TOLUIDINE-BLUE (B. A. S. F.; M. L. B.; Berlin).



Toluidine-blue or hydrochloride of *dimethyltoluthionine* is also nearly related to methylene-blue; it is manufactured in the same way as thionine-blue, but orthotoluidine is used instead of ethylmethylaniline. In its general character and tinctorial properties it also resembles the two preceding dyestuffs. It gives nearly the same reactions and is dyed in the same manner. The commercial article is also the zinc double salt.

NEW BLUE (MELDOLA'S BLUE).

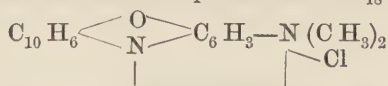
A number of blue basic dyestuffs, ranging in shade from reddish-blue to greenish-blue, are in the market under various names, which belong by their chemical constitution to the group of *oxazines* and are derivatives of *phenoxazine* or *anhydro-orthoxydiphenylamine*



compounds of tertiary aromatic amines, or of quinone-chlorimides, or of aromatic diamines on certain phenols, *e.g.*, betanaphthol. These colours resist the action of light fairly well. (Other oxazine dyestuffs produced in a more or less different manner (gallocyanin, resorcin-blue, &c.) belong to a different class of colours.)

The various commercial brands, such as **New Blue D** (Cassella), **Naphthylene-Blue R** (Bayer), **Fast Blue for Cotton** (B. A. S. F.,

Berlin), **Metamine-Blue** (Leonhardt), consist chiefly of the chloride of *dimethylphenyl ammonium betanaphthoxazine*. $C_{18}H_{15}N_2OCl =$



which is obtained by the action of nitrosodimethylaniline hydrochloride on betanaphthol. A number of other "new blues," &c., are produced in a similar way with nitrosodiethylaniline and possess essentially the same properties. We shall mention all these together, under the name of "new blue," by which they are most generally known. New blues are the salts of monacid bases, and yield leuco-products by reduction, from which the dyestuffs are regenerated by the oxidising action of the atmospheric oxygen. The commercial products are either crystals or dark-violet powders with bronze reflex, the dust of which violently attacks the mucous membranes. They are readily soluble in water with a violet-blue, and in alcohol with a blue colour. Addition of hydrochloric acid makes the aqueous solution bluer, and caustic soda produces a brown flocculent precipitate. Sulphuric acid dissolves the dyestuffs with a blackish-green colour, which becomes violet to blue on diluting with water.

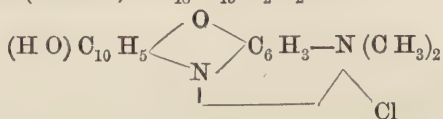
Application.—The new blues are dyed exclusively on cotton; they are not suitable for the animal fibres. It is best to dissolve the colour with the addition of some hydrochloric acid.

Cotton is mordanted with tannin (5 to 10 per cent.) and antimony in the usual way. Shades of inferior fastness are obtained by fixing the tannin in a bath of stannate of soda at $1\frac{1}{2}^\circ$ Tw. or stannic chloride (3° Tw.). Iron mordants are not recommended. The dye-bath is prepared with the necessary amount (3 per cent.) of colouring matter and 2 per cent. of hydrochloric acid (of the weight of the cotton). Enter the cotton at 30° and heat slowly to boiling; the bath will be exhausted. After dyeing, brighten by passing through very dilute hydrochloric acid, wash well and dry. If fastness to washing is not required the tannin may be fixed in a bath of basic alum. No acid must be used in dyeing or in brightening if the goods have been mordanted with alum.

New blues yield indigo shades, which are fairly fast to air and light, to acids and soap. By soaping, however, they become more violet and duller; they do not resist the action of alkalis. The colours serve in many cases as substitutes for indigo, and are used with advantage for topping vat-indigo.

New blues are sold in mixtures with methylene-blue and can be dyed by the same methods as the latter.

MUSCARINE (Durand). $C_{18}H_{15}N_2O_2Cl =$

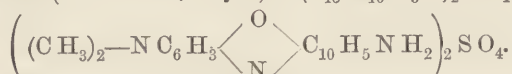


Muscarine or *dimethylphenylpara-ammoniumbetaoxynaphthoxazine chloride* is prepared by the action of nitrosodimethylaniline on the so-called alphasioxynaphthalene (2 : 7) (a derivative of betanaphthol). It is a salt of a monacid base, and gives on reduction a leuco-compound from which the original dyestuff is regenerated by the action of the air.

The commercial product forms a brown-violet powder, which is sparingly soluble in cold, readily in boiling water. The aqueous solution has a blue-violet colour and gives a blue-violet precipitate on addition of hydrochloric acid; caustic soda turns it yellowish-brown. Sulphuric acid dissolves the dyestuff with a bluish-green colour; the solution becomes on dilution with water at first blue, then violet, and finally yields a violet precipitate.

Application.—Muscarine is used in cotton dyeing and especially in calico-printing. Cotton is mordanted with tannin and antimony, and in dyeing the temperature is raised to about 80°.

NILE-BLUE (B. A. S. F., Bayer). $(C_{18}H_{16}N_3O)_2SO_4 =$



Nile-blue, the sulphate of *dimethylphenylpara-ammoniumalphaamido-naphthoxazine*, is formed by the action of nitrosodimethylmetaamidophenol on alphanaphthylamine. Nile-blue is the monacid salt of a diacid base; the hydrochloride is very sparingly soluble in water; hence this dyestuff is sold in the form of the sulphate. Nile-blue yields a leuco-compound, which is reoxidised by the air.

Nile-blue occurs in commerce as a dull-green crystalline powder with a bronze reflex, which dissolves sparingly in cold, readily in hot water, and in alcohol with a blue colour. From the aqueous solution the hydrochloride is precipitated on addition of hydrochloric acid in minute needle-shaped crystals, which appear violet in transmitted and green in reflected light. Caustic soda produces a flocculent dark red precipitate in the aqueous solution. Nile-blue dissolves in sulphuric acid with a brownish colour which changes, through green, into blue on diluting with water.

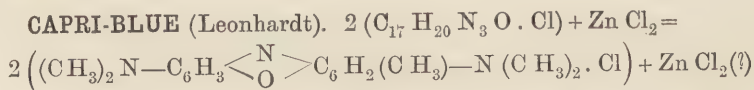
Application.—Nile-blue is a valuable product for the dyeing of cotton and silk, but not for wool. It yields shades similar to methylene-blue.

Cotton is mordanted with tannin and antimony and then soaped, as described on p. 453. Dye in a fresh bath and add the colour-solution gradually; after some of the dyestuff has been taken up heat slowly to 80° to fix the colour well, wash and dry. Beautiful light greenish-blue shades are obtained with very small amounts of dyestuff.

Nile-blue on cotton equals methylene-blue in fastness to light and soap. It is absolutely fast to chlorine, to acids, and even to alkalis (thus differing from the similarly constituted new blues).

Wool is not dyed with Nile-blue, since the dyestuff fades rapidly on this fibre.

Silk is dyed in boiled-off liquor and brightened with acetic or tartaric acid.

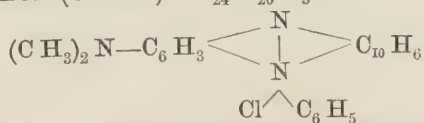


Capri-blue seems to be the product of the action of dimethylaniline on dimethylmeta-amidocresol, which is described in a recent patent application. Hence it would be *tetramethyldiamidophenyltoluoxazonium chloride*, combined as a double salt with zinc chloride.

Capri-blue G O is an olive-green powder, which dissolves in water with a greenish-blue colour. Hydrochloric acid first turns the aqueous solution cobalt-blue, then blue-violet, violet, and, lastly, crimson. Dilute caustic soda has no action on the aqueous solution. The solution in strong sulphuric acid is dichroic; green in thin layers, red in thick, crimson in gas-light by transmitted light. On diluting with water a crimson solution is obtained.

Application.—Capri-blue is dyed on **cotton** which has been mordanted with tannin and antimony. Enter cold, add the colour-solution gradually and heat to the boil, finish boiling, wash and dry. The shade is an extremely greenish blue, which resists light, soap, acids, and alkalies well.

Silk is dyed with Capri-blue with the addition of neutral soap. Enter lukewarm and bring to the boil; brighten with acetic acid. The shade is a beautiful blue-green (sea-green) in artificial light.



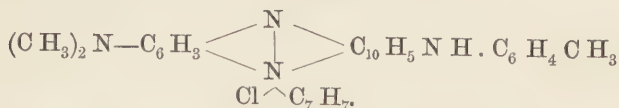
Neutral blue, or *phenyldimethylpara-amidophenonaphthazonium chloride*, is related to the safranines by its constitution. It is produced by the action of nitrosodimethylaniline on phenylbetanaphthylamine.

Neutral blue is furnished to the trade as a brown powder, which dissolves in water and in alcohol with a violet colour. On addition of hydrochloric acid the aqueous solution becomes more bluish; caustic soda produces a violet precipitate. The dyestuff dissolves in sulphuric acid with a brown-violet colour which becomes violet on dilution with water.

Application.—Neutral blue is useful for the production of compound shades on cotton; it is not suited for wool and silk. Cotton is mordanted with tannin and antimony and dyed in a neutral bath at

moderate temperatures. The shade is a dull blue, not fast to light or soap.

BASLE-BLUE R (Durand). $C_{32}H_{29}N_4Cl=$



Basle-blue, or *tolyldimethylamidophenotolylimidonaphthazonium chloride*, is also related to the safranines by its chemical constitution. It is produced by the action of nitrosodimethylaniline on ditolynaphthylene diamine (2 : 7). A very similar Basle-blue B B of a purer blue shade is produced with nitrosodimethylaniline and diphenylnaphthylene diamine.

Basle-blue forms a leuco-compound, from which the original dyestuff is regenerated under the influence of the air.

The commercial product forms a brown-violet crystalline powder, which is soluble in water with a blue-violet colour. The aqueous solution gives a blue flocculent precipitate with hydrochloric acid, and a blue precipitate soluble in pure water with strong caustic soda. The dyestuff dissolves in sulphuric acid with an olive-brown colour which becomes green and then blue on dilution with water, and finally yields a blue precipitate.

Application.—Basle-blue gives light reddish-blue to deep indigo-blue shades on cotton which has been mordanted with tannin; it is also dyed with good results on wool both in alkaline and in acid baths. It serves very well for topping indigo.

Cotton.—For light reddish-blue shades mordant with tannin and antimony and dye with 1 to 2 per cent. of Basle-blue at a moderate temperature. Then enter the dyed goods in a boiling-hot bath of sumach (20 per cent. sumach of the weight of the cotton) and soak for some hours; wring, and pass through a boiling-hot bath of antimony solution (2½ per cent. of tartar emetic); wash and dry. This after-treatment makes the shade exceedingly fast towards boiling alkalies and soap.

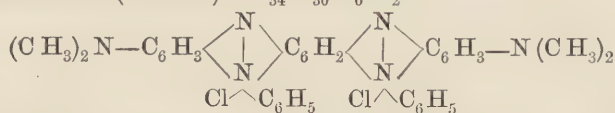
For the production of dark indigo-blue shades mordant with tannin (sumach) overnight and pass through a not too diluted solution of 6 per cent. copperas and ½ per cent. of chalk (of the weight of the cotton) for 15 to 30 minutes, hang some hours in the air without allowing the material to dry, wash, and dye with 2 to 4 per cent. of Basle-blue, hot or cold. By using more copperas and chalk (12 and 2 per cent. respectively) very dark shades are produced.

Basle-blue is distinguished by relative fastness to hot soaping and to light.

Wool.—(1) In acid bath; prepare the bath with 10 per cent. of Glaubersalt, 5 per cent. of sulphuric acid, and the required amount of

dyestuff. (2) In alkaline bath; prepare the bath with 5 per cent. of borax and 5 per cent. of soda ash and the required amount of dyestuff. In both cases enter the wool cold and heat to the boil, boil until the bath is exhausted, wash and dry. From light to deep reddish-blue shades are obtained; those dyed in alkaline appear fuller than those in acid baths. The colours resist boiling soap and alkalis very well.

INDAZINE M (Cassella). $C_{34}H_{30}N_6Cl_2 =$



Indazine M, or *tetramethyldiamidodiphenazinephenyl chloride*, is produced by heating nitrosodimethylaniline with that diphenylmetaphenylenediamine which is formed by the action of aniline on resorcin.

Isomeric products possessing similar properties—*e.g.*, *indazine F F*—are also in the market.

Indazine M is a blue powder with a bronze reflex, which dissolves in water and in alcohol with a violet-blue colour. Hydrochloric acid makes the aqueous solution bluer; and caustic soda produces a blackish-blue precipitate. Sulphuric acid dissolves the dyestuff with a blackish-green colour, which becomes blue on dilution with water.

Application.—Indazine M is chiefly dyed on cotton, but can be used with good results on wool and silk. It gives deep indigo shades, which are fast to acids and alkalis and resist soaping and milling very well, but are not very fast to light.

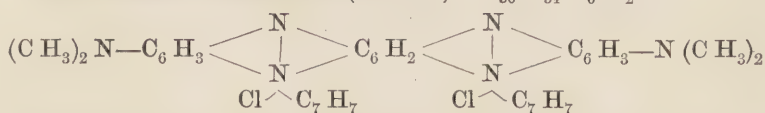
Cotton is mordanted with tannin and antimony (for dark shades with tannin and nitrate of iron), and dyed in a slightly acidulated bath, the temperature of which is slowly raised from lukewarm to boiling.

The shades are faster than those of new blue to soaping, but less fast to light.

Wool is dyed in a slightly acidulated boiling bath.

Silk is dyed in a bath of acidulated boiled-off liquor. Steel-blue to violet-blue shades are obtained, according to the concentration of the bath.

METAPHENYLENE-BLUE (Cassella). $C_{36}H_{34}N_6Cl_2 =$



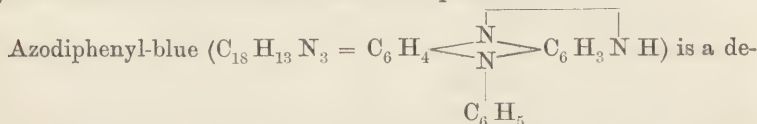
Metaphenylene-blue is homologous with indazine M; it is *tetramethyldiamidodiphenazineorthotolyl chloride*, and is produced in a similar way as indazine M, by heating nitrosodimethylaniline with that diorthotolylmetaphenylenediamine, which is formed by the action of orthotoluidine on resorcin.

Metaphenylene-blue resembles in its general chemical and tinctorial properties indazine M, and is applied in the same way as this dyestuff.

The commercial product forms a violet powder, which dissolves readily in water with a bright blue colour. Hydrochloric acid makes the aqueous solution slightly duller; caustic soda produces a blue-violet precipitate. The solution in concentrated sulphuric acid is dull blue, and is not altered in appearance by diluting with water.

THE INDULINES AND NIGROSINES.

By heating amidoazo-compounds with aromatic monamines a great number of blue dyestuffs are produced, which are called *indulines*; the simplest representative of these is *azodiphenyl-blue* or *induline B* ($C_{18}H_{13}N_3$), which is formed by heating amidoazobenzene and aniline hydrochloride in alcoholic solution under pressure to 160 C°.



These compounds are sparingly soluble in water. The indulines form monacid salts; with reducing agents they yield leuco-compounds, which are reoxidised by atmospheric oxygen.

A number of *soluble indulines* are produced by the action of aromatic diamines on amidoazo-compounds—e.g., *paraphenylene-blue*.

The *indulines of the naphthalene group* are formed by the action of aromatic monamines on azo- or nitroso-compounds of naphthalene substances or derivatives of alpha- and betanaphthoquinones. On account of the red shades these indulines yield in dyeing they are called *rosindulines*.

Nigrosines are dyestuffs which are related to the indulines, but dye greyish shades. They are formed when nitrobenzene or nitrophenol is heated with aniline, hydrochloric acid, and iron to 180°. Nigrosines and indulines are found in the bye-products of the manufacture of magenta.

The indulines are distinguished by great fastness to light and soap.

INDULINE, SOLUBLE IN SPIRIT.

Fast-Blue, Coupier's-Blue, Azodiphenyl-Blue, Indigen, Pelikan-Blue, Indophenine B (Bayer), Blue for printing (Berlin), Acetine-Blue (B. A. S. F.), Levuline-Blue (M. L. B.), Nigrosine.

Induline soluble in spirit is not a uniform substance; it consists of mixtures of various indulines, such as azodiphenyl-blue ($C_{18}H_{13}N_3 \cdot HCl$), the indulines $C_{18}H_{15}N_3 \cdot HCl$ and $C_{24}H_{18}N_4 \cdot HCl$, induline 3 B ($C_{30}H_{23}N_5 \cdot HCl$), and, possibly, induline 6 B ($C_{36}H_{27}N_5 \cdot HCl$).

These indulines are brought into the market in various forms.

(1) As violet-black or brown-black powders, not soluble in water, but soluble in alcohol with a violet-blue colour (induline soluble in spirit, &c.). (2) As pastes, containing substances which tend to make them soluble in water such as aniline, hydrochloric or acetic acid (indophenine B). (3) As a neutral blue-violet paste, which is partially soluble in water (blue for printing). (4) As solutions in levulinic or ethyltartaric acid or acetine, forming blue to violet-blue liquors (levuline-blue, acetine-blue).

Application.—The indulines serve as excellent substitutes for vat-indigo on account of their great fastness to soap and to light. They cannot compare, however, with indigo as to beauty of shade, especially in light tints.

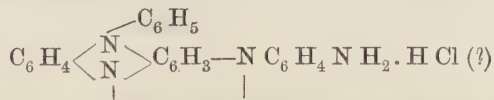
Cotton.—Induline soluble in spirit is not dyed on cotton; it can be fixed, however, on tannin and antimony mordant. Indophenine B is suitable for the dyeing of cotton by the following method:—Mordant with 3 per cent. of tannin and work for 30 to 60 minutes in a bath containing 10 per cent. of aluminium sulphate and 5 per cent. of stannate of soda (of the weight of the cotton). This bath is prepared as follows:—Dissolve the aluminium sulphate, add it to the mordanting-bath and, subsequently, add the stannate of soda, stirring well during mixing. The mordanting-bath must never react alkaline; such a reaction would indicate an excess of stannate of soda and must be corrected by adding aluminium sulphate; the bath is stirred well just before use. After mordanting, dye the cotton without washing in a fresh bath at the boil. The mordanting- and the dye-bath can be kept for further use. Fuller shades are obtained by passing the dyed goods through a solution of $\frac{1}{2}$ per cent. of potassium bichromate or nitrate of iron (of the weight of the cotton). Indophenine B yields in this way dark indigo shades, which are exceedingly fast to light, soap, and acids.

The other commercial products are valuable for calico-printing, but are not well adapted for dyeing, since they have to be fixed by steaming.

Wool is not dyed with these indulines.

Silk.—Very fast shades of indigo-blue are produced on silk with induline soluble in spirit. The dye-bath is prepared with 2 per cent. of sulphuric acid, the silk is entered at 50° and the temperature raised slowly to 80° , while the required amount of colour is gradually added.

PARAPHENYLENE-BLUE (Dahl). $C_{24}H_{18}N_4 \cdot HCl =$



Paraphenylene-blue or *amidophenylinduline hydrochloride* is produced by the action of paraphenylenediamine on amidoazobenzene. Paraphenylene-blue is a monacid salt. It yields on reduction a leuco-com-

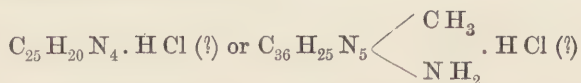
pound, from which the original dyestuff is easily regenerated under the influence of the air. It is changed by oxidising agents, such as potassium bichromate or ferric salts, becoming darker and insoluble in water ; use is made of this fact in dyeing to produce darker and faster colours.

Paraphenylene-blue forms a dark violet powder, which readily dissolves in water and in alcohol with a violet-blue colour. Hydrochloric acid makes the aqueous solution bluer, caustic soda produces a violet precipitate. Sulphuric acid dissolves it with a violet-blue colour which remains unchanged on diluting with water.

Application.—Paraphenylene-blue is especially suited for cotton dyeing, to produce deep indigo shades. It possesses extraordinary fastness to light and to soap. Cotton is mordanted in the usual way with tannin and antimony and dyed in a fresh bath ; enter cold and heat to the boil. The bath is exhausted. The shade can be saddened and made faster by passing the goods at 60° through a bath, containing $\frac{2}{10}$ per cent. of bichromate of potash, after which they may be turned again a few times in the original dye-bath, washed, and dried. If desirable for shading purposes, paraphenylene-blue may be dyed at a lower temperature and with addition of alum or acetic acid ; but in this case the bath is not exhausted.

The two following methods are also recommended ; by the manufacturers :—Mordant as usual with 4 per cent. of tannin, and then enter the cotton into a bath of acetate of chromium (1 to 1½ Tw.), to which the necessary quantity of tartar emetic (about 2 per cent.) is added. Leave the cotton in this bath at least two hours, then wash well and dye in the usual manner with paraphenylene-blue. The colours produced in this manner are then already purer and faster than those obtained by the previous method ; the beauty of the shades, and especially the fastness of the colours, may, however, be still further increased by adding to the bath, when it is nearly exhausted, a small quantity from the second mordant-bath (acetate of chromium). Or, mordant the cotton as usual with 4 to 6 per cent. of tannin, then soak it for 1 to 2 hours in a cold bath with 5 per cent. of stannous chloride, and turn for ½ to 1 hour in a cold bath containing 5 to 6 per cent. of stannate of soda. Then wash, and dye according to shade with 2 to 4 per cent. of dyestuff, and oxidise with bichrome, or pass through a bath of acetate of chromium.

TOLUYLENE-BLUE (Oehler).



The constitution of this new dyestuff has not yet been ascertained. It is produced by the action of paratoluylenediamine on induline, soluble in spirit.

Toluylene-blue forms a brown-violet powder, which is soluble in

water with an indigo-blue colour. A large excess of hydrochloric acid precipitates it from the solution as a polyacid salt. Caustic soda precipitates the colour-base in brown flakes. The dyestuff dissolves in sulphuric acid with a blue colour; on diluting with water a precipitate is formed which dissolves on addition of more water.

Application.—Toluylene-blue is a good substitute for vat-indigo on cotton; and it yields shades which are distinguished by superior fastness to light, soap, acids, and alkalis.

Cotton can be dyed without a mordant or after previous mordanting with tannin and antimony. Calcareous water must be corrected with acetic acid.

(1) *Dyeing of Mordanted Cotton.*—Mordant with tannin and antimony and prepare the dye-bath with 3 per cent. of alum or 4 to 5 per cent. of acetate of chromium (25° Tw.) and with the colour-solution; enter the cotton into the cold bath, work for 20 to 30 minutes cold, heat the bath to 50° C., and work until the bath is exhausted (about 30 minutes); finally boil for 15 to 20 minutes to fix the colour better, wash, and dry. The addition of 1 to 2 per cent. of stannic salt will produce brighter shades; light indigo shades are produced by an admixture of methylene-blue. Very dark indigo shades are obtained by subsequent saddening with bichromate, which may take place in the exhausted dye-bath; add to the bath while still hot $\frac{1}{2}$ to 2 per cent. of bichromate (of the weight of the cotton), turn for 15 to 20 minutes, and brighten by boiling the goods for 15 to 20 minutes in a soap-bath (the soap being 6 to 8 per cent. of the weight of the cotton).

(2) *Dyeing without Mordanting.*—This process is applicable for dark shades only. Prepare the dye-bath with the colour-solution (4 per cent. of toluylene-blue) and 6 to 8 per cent. of acetate of soda, and work the cotton in the unbleached state in this bath, as indicated above for mordanted goods. Subsequently, work the cotton for 15 minutes in a fresh boiling bath of 3 per cent. of bichromate and 1 per cent. of sulphuric acid or 3 per cent. of bichromate and 5 per cent. of copper sulphate, wash, and boil in 6 to 8 per cent. of soap.

Toluylene-blue can be topped with advantage by means of the direct cotton-colours, and this can be done in the soap-bath. When this is to be done with colours which are sensitive to copper no copper salt must be used in dyeing. On the other hand, the employment of copper sulphate is advisable when it is intended to top toluylene-blue with natural colours which form lakes with copper salts. Logwood, for example, gives a good coppery dark indigo shade. The original toluylene-blue bath may be used for the dyeing with logwood.

INDAMINE-BLUE PASTE* (M. L. B.)

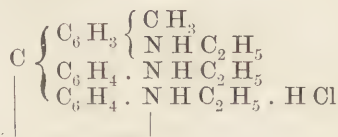
This dyestuff is sent out in form of a dark blue paste, the mode of preparation and composition of which have not been published.

* E. Ulrich, *Journ. Soc. Dyers and Col.*, 1890, p. 96.

It is also a soluble induline, and is applied in precisely the same way as toluylene-blue. It is very fast to boiling soap.

METHYL VIOLETS.

HOFMANN'S VIOLET, METHYL VIOLET R to 5 R, PRIMULA, DAHLIA. $C_{26}H_{32}N_3 \cdot HCl =$



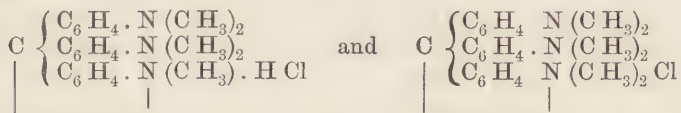
Hofmann's violet consists of various methyl- and ethyl-derivatives of magenta, which are produced by methylating or ethylating magenta with methyl or ethyl iodide, 1, 2, or 3 methyl- or ethyl-groups combining with the rosaniline-base. The hydroiodides thus formed are converted into the hydrochlorides, which are more freely soluble in water. The ethyl-derivatives dye a redder shade than those of methyl. The violets form salts, with one, two, and three equivalents of acids; the monacid salts only are stable in solutions. They yield leuco-compounds, from which the original dyestuffs are regenerated under the action of oxidising agents.

Violet 5 R, the reddest of the violets, shows the following reactions:—It is a green crystalline powder, soluble in water, with a magenta-red colour. The aqueous solution is turned yellowish-brown by hydrochloric acid, and gives a brown precipitate with caustic soda. Sulphuric acid gives a yellowish-brown solution which remains unchanged on diluting with water.

Application.—Hofmann's violet has been almost completely replaced by ordinary methyl-violet, and is used nowadays for white dyeing of wool only. It yields very pure red-violet shades, the reddest of the various methyl-violets. For methods of dyeing, see p. 496.

METHYL-VIOLET B and 2 B. Paris-violet.

The ordinary methyl-violets are mixtures of the hydrochlorides of various methylated pararosanilines, and consist chiefly of the two salts



Pentamethyl pararosanine hydrochloride.

Hexamethyl pararosanine chloride.

Methyl-violet is produced by the oxidation of dimethylaniline with cupric chloride. The more methyl groups there are in the product the bluer is the shade. In its general chemical character methyl-violet resembles Hofmann's violet. The commercial product is the hydrochloride, which occurs as a powder or in irregular lumps having a green

metallic reflex. It dissolves in water and in alcohol, as also in amyl-alcohol, with a violet colour. On addition of hydrochloric acid the solution becomes yellowish-brown; caustic soda gives a brown-red precipitate. Sulphuric acid dissolves the dyestuff with a yellow colour, which becomes, on diluting with water, at first yellowish-green, then greenish-blue, and, finally, violet.

Application.—See next page.

Methyl-violet is also used as an antiseptic, and is brought into the market for this purpose in a pure state under the name "*Pyoktanin*" by E. Merck (Darmstadt).

METHYL-VIOLET 6 B or BENZYL-VIOLET.

Methyl-violet 6 B or *pentamethylbenzylpararosaniline chloride* is a benzylated methyl-violet produced by the action of benzyl chloride on ordinary methyl-violet. Methyl-violet 6 B is very similar in its reactions and properties to methyl-violet B and 2 B.

Application.—See next page.

Methyl-Violet 3 B, 4 B, and 5 B are mixtures of the ordinary methyl-violet and methyl-violet 6 B. Methyl-violet 7 B and *marine-blue* (see p. 484) are mixtures of methyl-violets and methylene-blue. Mixtures of methyl-violets with malachite-green are met with in commerce under the names of *fast blue*, *indigo-blue*, &c., and mixtures with magenta are offered as *dahlia* and *primula*.

CRYSTAL-VIOLET (B. A. S. F.), or VIOLET 5 B (Bindschedler).



Crystal-violet is *pure hexamethylpararosaniline chloride* produced by the action of phosgene gas on dimethylaniline. It is brought into commerce in well-defined crystals, which contain 8 equivalents of water of crystallisation, and possess a peculiar greenish-brown metallic reflex. It dissolves very easily in water and in alcohol, with a deep violet-blue colour. Hydrochloric acid makes the aqueous solution first blue, then green, and finally yellow, with formation of polyacid salts; caustic soda produces a violet precipitate. Sulphuric acid dissolves the dyestuff with a yellow colour, which passes, on dilution with water, through olive-green and blue into violet. Crystal-violet possesses the advantage of great colouring power, extreme solubility, and of having no tendency to produce a bronze scum on the dye liquor or on the goods. It dyes a very bluish-violet of great purity.

Application.—See next page.

ETHYL-PURPLE (B. A. S. F.), or VIOLET 6 B (Bindschedler).

This dyestuff consists of *pure hexaethylpararosaniline chloride*. It is analogous in constitution to crystal-violet, and is similarly prepared by the action of phosgene gas on diethylaniline. The commercial product forms a green crystalline powder, which is easily soluble in water, with a violet-blue colour, and resembles crystal-violet in its

reactions and properties. It dyes the bluest violet shade of the various methyl-violets—still bluer than crystal-violet, and equal in purity to the latter.

Applications of the Methyl-Violets.—The various methyl-violets are very similar in their properties; they are readily soluble in water and dye from reddish- to bluish-violet shades on the vegetable and animal fibres. They are frequently used to brighten other colours by topping—*e.g.*, vat-indigo, logwood, and alizarin-violet.

The methyl-violets are not fast to light.

Cotton is mordanted with tannin and antimony and dyed in a fresh lukewarm bath as usual for magenta, &c. The shade is fairly fast to soaping. Dark shades are obtained by fixing the tannin with iron solutions, to which aluminium sulphate may be added for shading. The fixing-bath can be dispensed with if fastness to washing is not required. In the latter case the two following methods, which give brighter shades, may be used:—Boil the cotton for half an hour in a bath containing 10 per cent. of its weight of alum, wring without washing, and work it for 20 minutes at 50° to 60° in a bath containing 5 per cent. of its weight of soda crystals; rinse the cotton well and dye in a fresh lukewarm bath; wring and dry without washing. Or prepare for 10 kgs. (lbs.) of cotton a mordanting-bath as follows:—50 grms. ($\frac{3}{4}$ oz.) each of acetate of lead and tin crystals are dissolved together in 200 litres (20 galls.) of hot water; the mixture is allowed to stand until the precipitate formed has settled; then the clear liquor is run off and used. Enter the cotton into the clear liquor, heat to 70° or 80° C., turn for half an hour, then pass into a lukewarm bath of neutral soap, turn for 15 minutes and wash; dye in a fresh tepid bath, wring, and dry without washing. The other methods indicated in the introduction to this chapter—*e.g.*, with Turkey-red oil—may also be employed.

Wool is dyed with the methyl-violets in neutral or acid baths. Calcareous water is corrected with tartaric acid, bisulphate of soda, &c. When dyeing in a neutral bath without any additions, the bath is rapidly and completely exhausted; but the colour will not dye evenly. Better results are obtained by adding 10 per cent. of magnesium sulphate, or still better 5 per cent. of this salt and 5 per cent. of zinc sulphate to the neutral bath; but it is not exhausted in this case; the colour is taken up slowly and evenly and the shade is somewhat faster to milling, although even then but moderately fast. In an acid bath wool is dyed with 4 per cent. of alum or 2 per cent. of sulphuric acid, or best with 2 per cent. of sulphuric acid and 10 per cent. of magnesium sulphate. In all cases the wool is worked in the boiling bath for 20 minutes, and left in the bath until it has cooled to 60° or 70°. It is then taken out, washed, and dried.

Silk is dyed in an acid bath with, or without, boiled-off liquor. The silk is entered into the warm bath, the temperature raised to the

boil and maintained so for 15 to 20 minutes. After dyeing, the silk is washed and brightened in weak acid. For the red shades acetic or tartaric acid, for the blue shades sulphuric acid is used for acidifying and brightening; for crystal-violet and ethyl-purple, however, the organic acids are always preferable.

ALKALI-VIOLET (see p. 554, *Acid Colours*).

Alkali-violet is a sulphonated compound of the methyl-violet group. It belongs to the acid dyestuffs and will be fully described there.

It may be mentioned here that it can be dyed like the basic colours on cotton, which has been mordanted with tannin and antimony.

PHENYL-VIOLET. VIOLET SOLUBLE IN SPIRIT. PARMA or IMPERIAL VIOLET.

Phenyl-violet is a mixture of mono- and diphenylrosaniline, with very little triphenylrosaniline, in the form of hydrochlorides. It is obtained by the aniline-blue process (see p. 478), but less aniline is used, and the mixture heated for a shorter time than is required for blue.

Phenyl-violet forms a green granular mass, sparingly soluble in water, freely in alcohol with a violet colour. Hydrochloric acid gives a green flocculent precipitate; caustic soda throws down the colour-base, decolorising the solution. Sulphuric acid dissolves it with a brown colour; on dilution with water a flocculent precipitate is obtained.

Application.—Phenyl-violet is now little used; its shade is less bright than those of the methyl-violets, though faster to light and to milling.

Regina-purple (Br. S. & S.) is a similar product. It is obtained by a process similar to that used for phenyl-violet, but instead of aniline use is made of the “échappés” which distil over in the manufacture of magenta, and which consist chiefly of orthotoluidine. It may be considered as an orthotolyrosaniline.

The commercial product is the acetate, which is a green powder readily soluble in water with a red-violet colour. Hydrochloric acid makes the aqueous solution brown, on dilution blue. Caustic soda produces a brown precipitate. Sulphuric acid dissolves it with a brown colour, which remains on diluting with water.

Application.—Regina-purple is still used to a small extent in wool-dyeing, when a fairly fast but not very bright violet is required.

NEUTRAL VIOLET (Cassella). $C_{14}H_{14}N_4 \cdot HCl =$



Neutral violet, or *dimethyldiamidophenazine hydrochloride* closely

resembles neutral red, and, like it, belongs to the eurhodines (see p. 463). It is prepared by boiling nitrosodimethylaniline and metaphenylenediamine together in aqueous solution, and passing a current of air through the liquor. Neutral violet forms mono-, di-, and triacid salts; the monacid salts only are stable in solution. On reduction it yields a leuco-compound, from which the original dyestuff is regenerated by the action of the air.

Neutral violet forms a greenish-black powder, the dust of which irritates the mucous membranes. It dissolves in water with a red-violet colour, which is turned blue by an excess of hydrochloric acid; caustic soda produces a brown precipitate. Sulphuric acid dissolves it with a green colour, which passes on diluting through blue into red-violet.

Application.—Neutral violet is used on cotton only. It dyes a dull violet which is not fast to light.

Mordant with tannin and antimony, and dye in a neutral bath. Heat slowly to 50°.

FAST NEUTRAL VIOLET, PASTE (Cassella).

This is a new dyestuff, produced by the action of nitrosodimethylaniline on diethylmetaphenylenediamine. It has been introduced very recently and has not been studied yet either from a scientific or from a tinctorial point of view.

Application.—Fast neutral violet is recommended for the dyeing of cotton only on a mordant of tannin and antimony. It dyes a red-violet shade, for which good fastness to light, soap, and acids is claimed.

MAUVE, $C_{27}H_{25}N_4Cl$ or $(C_{27}H_{25}N_4)_2SO_4$.

Perkin's Violet, Rosolane, Mauveine, Chrome-Violet, &c.

This compound possesses great historical interest, since it was the first aniline dyestuff introduced into commerce, and was the immediate cause of the grand development of the aniline industry. It was invented in 1856 by W. H. Perkin, to whom the honour is due of being the originator of the present aniline industry. The formation of the dyestuff was observed as early as 1834 by Professor Runge of Berlin; at that time, however, coal-tar and aniline had not received the attention that was given to them twenty years later, so that Runge was unable to convince capitalists of the importance of his discovery, and, owing to lack of funds, did not succeed in introducing it into practical use.

Perkin obtained the dyestuff, mauve, by oxidising aniline-oil containing toluidine with chromic acid, and this is still the general method of manufacture. Mauve belongs to the safranines; its exact constitution is not known.

The commercial product is the hydrochloride or sulphate. It occurs as a red-violet paste; or, in crystals, which are sparingly soluble in

cold, more freely in hot or acidulated water, with a violet-red colour. Hydrochloric acid does not alter the aqueous solution; caustic soda produces a blue-violet precipitate. Sulphuric acid dissolves the dyestuff with an olive-green colour; the solution becomes on dilution with water at first blue and then violet-red.

Ethylated mauve has been brought into commerce under the name of *dahlia*, which closely resembles mauve.

Application.—Mauve had almost disappeared from the market, when the fashion of the summer of 1891 brought it into general use again. It dyes a dull violet of the shade of the British penny stamps, which are printed with mauve. In the production of bright greys it is used as a substitute for orchil and ammoniacal cochineal.

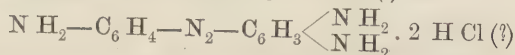
Mauve is faster to light than the other aniline-violets, and it is applied in the same way as they are, to the various fibres. Although it does not require a mordant itself, it may be dyed on mordanted materials for the production of compound shades.

PARAPHENYLENE-VIOLET (Dahl).

This new product belongs to the class of the "rosindulines," and is formed by fusing paraphenylenediamine with azo-compounds of alphanaphthylamine in the presence of benzoic acid. The dyestuff has not been studied yet and its exact composition is not known.

Application.—Paraphenylene-violet is used in cotton-dyeing and printing, and is applied in precisely the same way as paraphenylene-blue (see p. 491). It is distinguished by superior fastness, but it does not equal the blue in this respect.

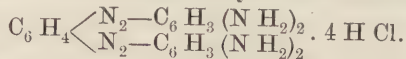
BISMARCK-BROWN. $C_{12}H_{13}N_5 \cdot 2HCl (?) =$



Manchester-Brown, Phenylene-Brown, Vesuvine, Canelle, Leather-Brown, &c.

Bismarck-brown is *triamidoazobenzene hydrochloride* produced by diazotising metaphenylenediamine.

Recent researches make it appear possible that Bismarck-brown is a tetrazo-compound formed by the action of one equivalent of diazotised metaphenylenediamine ($C_6H_4 \begin{matrix} \swarrow N_2 Cl \\ \searrow N_2 Cl \end{matrix}$) on two equivalents of metaphenylenediamine. In this case the dyestuff would be



Similar products are obtained by diazotising toluenylenediamine; they dye redder shades of brown. Bismarck-brown is a diacid (or tetracid) salt, which is converted by reducing agents into phenylene diamine and triamidobenzene, not into a leuco-compound.

The commercial product is a dark brown powder, soluble in water, with a brownish colour. Hydrochloric acid makes the solution more

yellowish, and caustic soda produces a brownish flocculent precipitate. Sulphuric acid dissolves the dyestuff with a brown colour, which is turned brownish-yellow on dilution with water.

Application.—Bismarck-brown resembles chrysoidine (see p. 467), both chemically and in its application. It dyes a pure brown, similar to catechu. The dyestuff has been employed to a great extent on the various fibres, and is still used in great quantities. It has, however, lost much of its former importance, as it is neither fast to light, nor soap, nor milling. It is largely used in the dyeing of leather.

Bismarck-brown should be dissolved in water free from lime at about 80° C. The solution must not be kept for a long time, since it decomposes spontaneously.

Cotton.—Bismarck-brown is applied in the same way as chrysoidine. It can also be fixed on tannin and iron. The shade becomes redder if alum is added to the dye-bath. Catechu is brightened by topping with Bismarck-brown. The dyestuff is useful for the production of compound shades in combination with the other basic colours.

Wool is dyed with Bismarck-brown as with chrysoidine. For a full shade 5 to 8 per cent. of dyestuff are required; the dye-bath is not exhausted. An addition of alum or aluminium acetate to the dye-bath makes the shade redder.

Silk is dyed by the same method as is described under *Chrysoidine*.

Havana-Brown is a mixture of Bismarck-brown and grenadine; it is applied in the same way as Bismarck-brown.

NEW GREY (Bayer). NIGRISINE, MALTA-GREY (Poirrier).

The composition and constitution of this dyestuff are not yet known. It is produced by boiling the aqueous or alcoholic solutions of nitrosodimethylaniline hydrochloride.

METHYLENE-GREY (M.L.B.), prepared by the oxidation of para-amidodimethylaniline, is identical with, or very similar to, the above dyestuff.

Alsace Grey (Fischesser) is also related to these products.

These dyestuffs have not yet been investigated thoroughly, and are probably not always uniform substances.

New grey forms a greyish-black powder, which dissolves in water with a reddish-grey colour. Hydrochloric acid makes the solution bluish-grey. Caustic soda produces a dark grey precipitate. Sulphuric acid dissolves it with a greyish-yellow colour which becomes reddish-grey on dilution with water.

Application.*—New grey is a valuable dyestuff for the dyeing of cotton and of cotton and silk mixed goods, and especially in calico-printing. It dyes a pure grey, and is very fast to light and soap. Calcareous water is corrected with hydrochloric acid.

* Th. Baumann, *Journ. Soc. Dyers and Col.*, 1890, p. 96.

Cotton is mordanted with tannin and antimony and dyed in a neutral bath, the temperature of which is gradually raised during one hour.

New grey can also be dyed without a mordant on cotton, even in the presence of hydrochloric acid. In this case it is steamed or aged after dyeing and then passed through a bichromate bath ($\frac{1}{2}$ per cent. solution) at 60°. The shade is more reddish than on tannin mordant. The addition of acetic acid to the dye-bath makes it bluer.

Silk and cotton and silk mixed goods are dyed in a neutral bath without mordants.

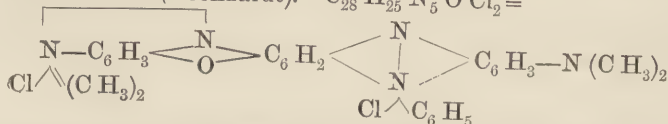
NIGROSINE (SOLUBLE IN SPIRIT). Silver-Grey, Steel-Grey

Nigrosine is a product similar to induline B. It is not a homogeneous substance and its composition is not known. It is prepared by melting a mixture of nitrophenol with aniline and aniline hydrochloride in the presence of iron.

The nigrosine of commerce is a greyish-black powder soluble in alcohol but not in water. It resembles induline.

Application.—Nigrosine dyes fast shades of bluish-grey. It is not used much in dyeing, since it yields light shades only; but it is used to some extent in printing cotton and silk piece goods and in leather dyeing. It is applied to the various fibres in the same way as induline, soluble in spirit.

FAST BLACK (Leonhardt). $C_{28}H_{25}N_5OCl_2 =$



Fast black is the product of the reaction of nitrosodimethylaniline with metaoxydiphenylamine. It forms a black powder, which is soluble in water with a violet-black colour; the aqueous solution gives a black precipitate on addition of hydrochloric acid, while caustic soda produces a violet-black precipitate. The solution in sulphuric acid is almost black, and becomes violet-black on diluting with water.

Application.—Fast black is dyed on cotton mordanted with tannin and antimony. It produces a blue-black shade, which is moderately fast to soap, and fairly fast to light.

ACID COLOURS.

The acid colours may be divided into three groups according to their origin and chemical constitution.

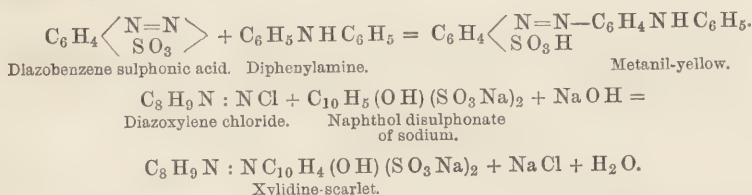
- (1) Nitro-compounds.
- (2) Azo-compounds.
- (3) Sulphonated basic colours.

All acid colours possess a distinct acid character and are dyed from acid baths, as is indicated by their name.

The first group, the nitro-compounds, owe both their acid character

and their tinctorial properties to the presence of several nitro-groups in their molecule. In addition to the "chromophorous" nitro-groups they contain, as "auxochromous" groups, hydroxyl (OH)—*e.g.*, picric acid, $C_6H_2(NO_2)_3(OH)$, or the imido-group (NH), as in aurantia, $[C_6H_2(NO_2)_3]_2(NH)$. The nitro-compounds are prepared by the action of nitric acid on certain phenols, such as phenol or naphthol; or on secondary aromatic amines—*e.g.*, diphenylamine. With the exception of naphthol-yellow S and Schoellkopf's brilliant yellow, none of these dyestuffs are sulphonated compounds. Like the other acid colours the commercial products are sold in the form of their alkaline salts (picric acid excepted).

The second group, the azo-compounds, are, without exception, sulphonic acids of amido- or oxyazo-compounds, the azo-group ($-N=N-$) being the chromophor and the group (NH₂) or (OH) respectively, the auxochromous group. The acid azo-colours are produced (like the tetrazo-compounds) by combining diazotised aromatic amines and their sulphonic acids with aromatic amines or phenols or their sulphonic acids, *e.g.* :—



Most of the acid azo-colours contain one azo-group only; some of the tetrazo-compounds, however, also belong to this class, and generally speaking the latter cannot be strictly divided into acid colours and direct cotton colours, since most of the tetrazo-colours can be dyed on the animal fibres by the same methods as the true acid colours, although not always with satisfactory results.

The third group consists of the sulphonic acids of certain bases which are colouring matters by themselves, and contain both the chromophorous and the auxochromous groups. The bases are sometimes employed as basic dyestuffs, *e.g.*, magenta or aniline-blue; in many cases, however, their insolubility in water, cost of production, or other causes, prevent their application in dyeing without being sulphonated, as is the case with the bases of the acid greens and acid violets, &c. The chromophors of this group are generally in accordance with the origin of the dyestuffs, the same as those of the basic colours. Most of these dyestuffs are derivatives of triphenylmethane; notable exceptions are tartrazin, quinoline-yellow, azocarmin, thiocarmin, and the indulines. By the entrance of the sulpho-group into the basic compound an acid character is imparted to the latter, and the tinctorial properties become greatly changed. The shade remains about the same, but it becomes greatly reduced

in colouring power; on the other hand, the fastness to light is increased. In addition, the dyestuffs lose by sulphonating the property of forming lakes with tannic acid, and cannot be fixed on cotton or linen like the original substances; for their fixation on the animal fibres an acid bath is required.

The various acid colours are sold in the form of their alkali salts; a few—*e.g.*, the patent blues—in the form of their lime salts. Picric acid is an exception; it is sold in the free state, owing to the picrates being explosive substances.

The acid colours are decolorised by the action of acid reducing agents, but they are affected in very different ways. The nitro-compounds are converted into amido-compounds, from which the original colouring matter cannot be regenerated. The azo-compounds are decomposed by the breaking up of the azo-group and cannot be linked together again in a simple manner. Lastly, the dyestuffs of the third group form leuco-compounds, from which the original colouring matter is more or less easily regenerated by oxidation.

The nitro-compounds dye yellow shades on wool and silk; they are not used in cotton dyeing. With the exception of the naphthol-yellows and brilliant yellow they find but limited and decreasing application. The azo-colours produce principally yellow, orange, red (from yellowish to bluish-red), and brown shades; lately some violet and very important black colours have been produced. No pure green colouring matters have yet been obtained, the green shade of which is due to the azo-group; azogreen is no exception to this rule, since the triphenylmethane-combination in it is its green chromophor, and the azo-group occupies a subordinate position. Of the third group, red, yellow, green, blue, and violet colouring matters are met with in commerce. Some colouring matters of the second and third groups—*e.g.*, the crocein scarlets and soluble blues—are used in cotton-dyeing, but their most extensive use is in the dyeing of wool and silk. The acid colours are of greatest importance in the dyeing of wool.

The distinction of the acid colours as a separate group is based on practical requirements, not on strictly scientific principles. On the one hand there is no sharp line of demarcation between them and the direct cotton colours, and on the other hand, the acid colours and mordant colours are frequently related to each other, a number of dyestuffs belonging practically to two of these three groups or even to all of them, as is, for instance, the case with cotton-yellow G. A few, like the soluble blues, can also be dyed like the basic colours. The common characteristic property of the acid colours is that they are dyed on wool in an acid bath and that they can be mixed with each other to produce compound shades.

In this chapter will be described the acid dyestuffs which are principally dyed in acid baths without the aid of mordants, while those, like the cloth-reds, the importance of which lies in their property

of producing shades fast to milling on *mordanted* wool will be described with the *mordant colours*. Those which dye cotton tolerably fast to washing have been described as *direct cotton colours*.

Methods of Dyeing with the Acid Colours.—The acid colours, with very few exceptions, cannot be fixed on cotton or linen so as to resist washing. If precipitated in these fibres as metallic lakes with the aid of salts of aluminium, tin, &c. (similarly to the mordant colours), the lakes are decomposed by water and the colour is extracted; the soluble blues or cotton-blues resist washing moderately well. Of the other acid colours the croceïn-scarlets and allied colours only—*i.e.*, the azo-compounds prepared by combination of amidoazobenzene or amidoazotoluene with betanaphthol sulphonic acid (B.), or the so-called gamma acid (p. 319) or alphanaphthol disulphonic acid (Sch.)—are of some importance in cotton dyeing since they resist light better than the benzidine colours and are not sensitive to acids. For this reason they are still employed in cotton dyeing in spite of their inferior fastness to washing. The acid colours have never been used to any large extent in the dyeing of linen, but they find application on jute.

It is principally the wool fibre on which the acid colours find application, and on this material they are dyed to a very great extent, owing to the simple and comparatively permanent manner in which they can be fixed on this material; the wool fibre mainly possesses a natural affinity for acid colours, acting as a base and forming more or less insoluble lakes with them. For the fixation of the acid colours on wool an acid bath is required, and this fact is usually explained by the supposition that the acid is necessary to set the colour acid at liberty and to enable it to combine with the wool. From investigations made on this subject,* however, it appears that the acid which is added to the dye-bath not only acts on the dyestuff, but also chemically changes a portion of the wool so as to render it capable of combining with the colour acid. Wool was boiled with 10 per cent. of its own weight of sulphuric acid and then boiled out 9 times with 100 times its own weight of distilled water, until the water was absolutely neutral to methyl-orange. In dyeing with 2 per cent. crystal-scarlet *without* any addition of acid, the wool showed a considerably fuller and more even shade than another pattern dyed with 2 per cent. of the same dyed with an addition of $2\frac{1}{2}$ per cent. sulphuric acid. On the other hand, if the dye-bath was made up with sufficient sulphuric acid to neutralise the sodium in the dye—0.2 per cent. sulphuric acid for 2 per cent. crystal scarlet—a light shade only was obtained; nor was double this amount sufficient to produce a full shade, and practical experience has shown that the minimum amount necessary is 2 to 3 per cent. or from 20 to 30 times as much as would be necessary to liberate the free colour acid.

The acid colours possess less importance for silk than for wool,

* *Journ. Soc. Dyers and Col.*, 1888, p. 107.

because few of them can be fixed on silk fast to washing. It seems that the basic properties of the silk fibre are too feeble to form stable compounds with the colour acids, and that the salts which are formed between the two substances are decomposed by water. The basic colours which are retained permanently by the comparatively strong acid powers of this fibre are more suitable for silk dyeing than the acid colours.

The acid colours vary in fastness to light; none is perfectly fast; but a great number of them resist light fairly well. Their resistance towards other influences, such as washing, milling, or rubbing, as a rule, is greatest on wool, but varies even on this fibre.

Dissolving of the Colours.—The acid colours dissolve (with a few exceptions) freely in hot water, and require about 25 to 50 times their own weight of water for solution. It is best to use distilled water, although, as a rule, hard water is not so injurious in the dyeing with the acid colours as with most other dyestuffs, because the dyeing proceeds in an acid bath, and the lime-lake which may have been formed is afterwards decomposed by the acid. The colours should be well dissolved in boiling water, and the solutions filtered before use.

The colours may be dissolved in tin vessels without injurious effect. It must be noted, however, that most of these dyestuffs are reduced by stannous salts, and, therefore, the *acidified* solutions of the colours should not be in contact with tin, and the dyeing should not take place in tinned vessels.

The acid colours produce beautiful and delicate hues, but they do not possess great tinctorial power. For a full shade on wool, in most cases about 3 per cent. of colour are required.

The methods which are best suited for the application of the different dyestuffs are indicated in the special descriptions; in the following are given various methods which are more or less generally employed:—

Dyeing of Cotton with the Acid Colours.—The dye-bath is used as concentrated as possible to produce full shades; it is never exhausted by the cotton. Both the mordant- and dye-liquors are used continuously and freshened up regularly; if the dye-bath should become turbid, the clear liquor is drawn off for further use; the precipitate is boiled out with water as long as it yields colouring matter, and the extract is added to the clear liquid after filtering. The shades which are produced by any one of these methods are not fast even to a light soaping, but they resist light moderately well.

First Method.—The dye-bath is made up with common salt to stand at 5° to 7° Tw., and an excess of colouring matter is added. The goods are boiled in the solution and dried without washing. Light and fugitive shades only can be produced in this way.

Second Method.—Cotton is impregnated with a solution of soap, to which some gelatine has been added, and dyed without washing.

(This preparation with soap and gelatine is frequently omitted.) The dye-bath is prepared with 10 per cent. of alum and 1 per cent. of acetic acid (of the weight of the goods) and kept very concentrated, common salt being added with advantage; the temperature is gradually raised to the boiling point, and finally the goods are dried without washing. The colour is not at all fast to washing, and resists the action of light less than when dyed by one of the following methods.

Third Method.—Cotton is mordanted in a bath which has been prepared by dissolving 1 kg. (1 lb.) of alum, and $\frac{1}{2}$ kg. ($\frac{1}{2}$ lb.) of soda crystals, in 200 litres (20 galls.) of water for every 10 kgs. (10 lbs.) of cotton. The goods are worked for half an hour in this bath and then allowed to soak 3 to 5 hours longer, wrung out and dyed (without washing) in a separate dye-bath at 40° to 50° ; after 45 minutes working they are taken from the bath, wrung out, and dried without washing. The cotton may be impregnated with tannin before it is mordanted with alum; it is said that the shades thereby become faster to washing.

Fourth Method.—The cotton is steeped for 2 to 3 hours in a lukewarm bath, prepared by dissolving $\frac{1}{2}$ kg. ($\frac{1}{2}$ lb.) of stannate of soda in 200 litres (20 galls.) of water for every 10 kg. (10 lbs.) of cotton, wrung out, and steeped for 2 hours in a bath of basic alum. The preparation of the alum-bath and the subsequent dyeing proceed exactly as in the previous method.

Fifth Method.—The cotton is soaped in a warm soap-bath to which some gelatine has been added, and worked for half an hour in a cold bath of stannic chloride, wrung, and worked for another half-hour in a bath of basic alum prepared as before. It is then dyed as by the previous methods.

Several colouring matters, notably Biebrich scarlet, fast red A, and azococcin 2 R, form insoluble precipitates with alum; before dyeing cotton which has been mordanted with alum in such dyestuffs it should be rinsed in cold water, and some acetic acid should be added to the dye-bath.

Many attempts have been made to *animalise* the cotton in order to make it take up the acid dyes like wool and silk, but so far no process has been devised which is of any practical importance. Of the methods proposed, the following may be mentioned:—Treatment with tannic acid and, subsequently, with gelatine; impregnating with albumen solution and steaming; treatment of the cotton with ammonia and zinc or calcium chloride under pressure (L. Vignon, see p. 21); impregnating with a solution of wool in caustic soda, and, subsequently, passing through dilute sulphuric acid.

Linen can be dyed with the acid colours in precisely the same way as cotton, but it requires faster shades than can be obtained with these materials.

Dyeing of Jute with the Acid Colours.—As little acid as possible, preferably acetic acid, is used for the dyeing of jute with the acid colours. In the case of dyeing with colours the free acid of which is very soluble jute is mordanted with basic alum; if the colour acid is not freely soluble no mordanting is necessary; often some alum is added to the dye-bath.

The acid colours are not very important for the dyeing of jute.

Dyeing of Wool with the Acid Colours.—*First Method.*—The simplest process of dyeing wool with the acid colours is to prepare the dye-bath with the required amount of dyestuff and 2 to 4 per cent. of sulphuric acid, and to boil the wool in this bath. Many dyestuffs, however, give very uneven results under these conditions by combining too rapidly with the wool fibre, and it is necessary to moderate the action of the sulphuric acid, causing the fibre to take up the colour more slowly and evenly. This is effected to some extent by adding Glaubersalt (10 to 30 per cent. of the weight of the wool) to the dye-bath.

Second Method.—A better way is to introduce the material into the warm bath, to which has been added the required amount of colouring matter, to heat up to the boiling point, and gradually add the sulphuric acid in small portions to the *boiling* bath, turning frequently all the time. In place of sulphuric acid alone a mixture of 2 to 5 per cent. of sulphuric acid and 10 to 30 per cent. of Glaubersalt, or, better, 5 to 10 per cent. of bisulphate of soda can be used; the action of this mixture or compound respectively is more moderate and regular than that of sulphuric acid alone (see p. 189). The method of adding the colour solution gradually in several small portions to the bath is not so well adapted to produce even shades in the dyeing with these colouring matters as with the basic colours.

Third Method.—More brilliant colours are produced by making up the dye-bath with the colour solution and 5 to 8 per cent. bisulphate (or 2 to 3 per cent. sulphuric acid and 10 per cent. Glaubersalt), and adding either 1 to $1\frac{1}{2}$ per cent. stannic chloride (60° Tw.) or 6 to 8 per cent. alum; the wool is introduced at 40°, and the bath heated more or less rapidly to the boil, and kept boiling as long as required.

Since the azo-colours are reduced and destroyed by stannous chloride, the presence of this compound in the tin solution must be strictly avoided.

Fourth Method.—A number of dyestuffs, notably the fast reds and fast blues are difficult to dye level. In the dyeing with these colours a very gradual action of the acid is necessary to obtain even shades, and the following process is advisable:—The dye-bath is prepared with 3 kgs. (3 lbs.) sodium acetate for every 1,000 litres (100 galls.) of dye-liquor, then the required amount of colouring matter is added and the wool is boiled in the bath for 2 hours; at last, as much sulphuric acid or sodium bisulphate as may be necessary for the development of the

shade is added gradually; thus the dye-bath is fairly exhausted. If the dye-bath is used continually, or the goods are not easily dyed through, it is better not to add the acid to the dye-bath, but to pass the goods afterwards through a separate acid bath for developing. (See *Alkali-blue* or *new blue of Hoechst*.)

Fifth Method.—The bath is prepared with 10 per cent. acetic acid (of the weight of the wool), the colour solution is added and the dye-liquor nearly neutralised with ammonia so that it remains only slightly acid; the goods are boiled in this solution; after 2 hours boiling, 10 per cent. more acetic acid are added and the boiling is continued for some time (in the acidulated bath most other dyestuffs—acid or basic—can be dyed). The bath is used continuously, being nearly neutralised after each operation with ammonia. After 4 to 5 operations sufficient acetic acid is in the bath and sulphuric acid may be used for acidulating; the latter combines with the ammonia and liberates acetic acid.

Sixth Method.—Instead of the acetate of ammonia which is formed in working by the previous method sulphate of ammonia can be used. This salt decomposes slowly on boiling, ammonia is driven off with the steam and sulphuric acid is liberated very gradually in the dye-liquor. Thus very good results are obtained with colours which are otherwise very difficult to dye level. The bath is made up with 20 to 25 kgs. (20 to 25 lbs.) ammonium sulphate for 1,000 litres (100 galls.) of dye-liquor, the colour solution is added and the wool boiled in this bath for $2\frac{1}{2}$ hours. After this time the bath is generally sufficiently acid for dyeing with all other acid colours; sometimes it is better to add a little acetic acid to develop the shade completely. If the bath is to be used continuously it is neutralised before the next operation with ammonia.

Seventh Method.—Alkali-blue requires a special procedure in dyeing which is described in connection with this colouring matter (p. 545).

The fastness of the acid colouring matters to light, milling, &c., on wool differs greatly. Most of the acid greens and acid violets are very fugitive to light, whereas many of the azo-colours are fairly fast. Many of the colours resist soaping and milling fairly well; they are, however, generally stripped to some extent and liable to bleed, this defect being common to all direct-dyeing colours; by boiling with alkaline liquors they are removed from the fibre (see below). Some of the acid colours are prone to rub if the dye-bath is not exhausted; hence it is better in most cases not to use an excess of colouring matter; good rinsing of the material after dyeing will obviate this defect to some extent. As a rule the acid colours are not sensitive towards the action of dilute acid, most of them resist alkalies well; many, however, principally those of the third group, are decolorised or greatly altered by alkalies.

It is sometimes desirable to remove the colour from the fibre; the best way is to boil the goods in a solution of ammonium acetate which

strips the colour slowly without damaging the material. By boiling the goods for 15 or 20 minutes with a small quantity of soda ash or ammonia, the acid colours are removed more thoroughly and rapidly; but the wool fibre is always deteriorated to some extent by the alkaline liquor. After this treatment the material is to be rinsed in water and, subsequently, boiled with some acid before it can be dyed again with acid colours.

Dyeing of Silk with the Acid Colours.—Silk is usually dyed with the acid colours in a bath containing about 10 per cent. (of the volume of the bath) boiled-off liquor, which is slightly or distinctly acidulated with sulphuric or acetic acid. Sometimes the colour solution is added at once to the bath and the goods dyed at the boil; in other cases, it is necessary to add the colour solution gradually or to heat the bath slowly. After dyeing, the silk is washed in water, brightened in very dilute sulphuric, acetic, or tartaric acid, and dried without further washing. In some cases silk is dyed with acid colours with the addition of acetic acid only, no boiled-off liquor being used.

The acid colours are not fixed very well on silk; most of them, notably picric acid, are removed even by washing with water. It seems that silk possesses only slight affinity towards these compounds, the basic properties of the silk fibre being weaker than those of the wool fibre.

N.B.—The reactions and the constitution of these colours are indicated in the same manner as those of the direct cotton colours (p. 413).

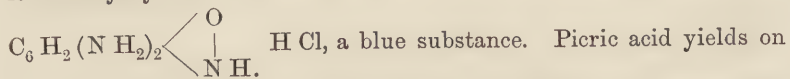
NITRO-COMPOUNDS.

PICRIC ACID. $C_6H_2(NO_2)_3OH$.

Picric acid or symmetrical *trinitrophenol* is produced by heating a solution of phenol in a mixture of concentrated sulphuric and nitric acid. The product is purified by recrystallising from water.

Picric acid forms pale-yellow crystals which melt at $122^{\circ}5$ and burn on being heated rapidly. It is sparingly soluble in cold, more freely in hot water, and readily soluble in alcohol or ether. The solution has a greenish-yellow colour and a very bitter taste. HCl has no action on the solution; $NaOH$ makes the aqueous solution dark yellow; solution in H_2SO_4 , yellow; on diluting, light yellow.

Picric acid is reduced by ammonium sulphide to *picraminic acid*, $C_6H_2(NH_2)(NO_2)_2(OH)$. By complete reduction it is converted into colourless *triamidophenol*, $C_6H_2(NH_2)_3OH$, which is transformed by hydrochloric acid into diamidoquinoneimide hydrochloride,



boiling with potassium cyanide a brown-red solution of *potassium iso-*

purpurate, $K C_8 H_4 N_5 O_6$. The alkaline salts of picric acid crystallise well and are explosive, especially the potassium salt.

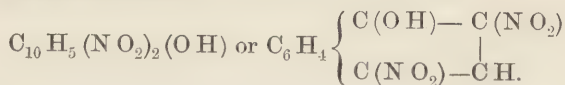
Application.—Picric acid does not dye the vegetable fibres. It was formerly an important yellow dyestuff for the dyeing of silk and wool; but it has been almost completely replaced by the naphthol-yellows, fast yellows, &c. Picric acid is still used in silk dyeing for its greenish-yellow shade and for its great tinctorial power. It is, however, extremely fugitive; soap and even water strip it from the fibre; and by the action of air and light it soon becomes dull and brownish. In addition, the colour is volatile, and sublimes slowly from the fibre even at the ordinary summer temperature. It is little used as a self-colour, but principally for shading blues and greens. Picric acid converts the animal skin into leather, and at the same time dyes it yellow; it is used in leather dyeing.

Wool is dyed with 1 to 5 per cent. of picric acid and with the addition of 2 to 3 per cent. of sulphuric acid, or 6 to $7\frac{1}{2}$ per cent. of alum. Enter cold, heat to the boil in 15 minutes, and dye 15 minutes at the boil; dry without rinsing. The bath is not exhausted. The greenish-yellow shade is not at all fast to light, water, soap, milling, or rubbing.

Silk is dyed with the addition of 1 to $1\frac{1}{2}$ per cent. sulphuric acid or 3 to 5 per cent. of acetic acid, or in a bath of acidulated boiled-off liquor. Enter cold, heat during one hour to 50° or 60° , and dry without rinsing. One-tenth per cent. of dyestuff gives a distinct straw-yellow tint, four-tenths per cent., lemon-yellow, and 1 to $1\frac{1}{2}$ per cent. full greenish-yellow shades, which are also extremely fugitive.

NAPHTHOL-YELLOW. MARTIUS-YELLOW.

Manchester-Yellow, Naphthalene-Yellow, Naphthylamine-Yellow, Aniline-Yellow.



Naphthol-yellow is the sodium, or ammonium, or calcium salt of *dinitroalphanaphthol*. It is prepared by dissolving alphanaphthol in sulphuric acid, and heating the solution with nitric acid.

Yellow or orange tablets or crystalline powder; aqueous solution, golden-yellow; HCl , light-yellow precipitate; $NaOH$, soluble precipitate; solution in H_2SO_4 , yellow; on diluting, light-yellow precipitate. Dinitronaphthol, the acid of naphthol-yellow, melts at 138° , and forms by reduction diamidonaphthol. The dry sodium salt of dinitronaphthol explodes on heating, the ammonium salt burns off quietly.

Application.—Wool is dyed as with picric acid. Less acid, however, is used, preferably 3 to 4 per cent. acetic acid, since an excess of acid gives rise to unevenness.

Silk is also dyed as with picric acid; the best way is to use a boiled-off liquor or soap-bath which has been acidulated with acetic acid. After dyeing the silk is rinsed, brightened, and dried.

Naphthol-yellow yields lemon-yellow to orange-yellow shades, which are not fast to milling or rubbing. The colour is moderately fast to air and light; it fades and becomes duller on exposure, but does not change much. The dyestuff is volatile and evaporates from the fibre, even at the ordinary summer temperature.

NAPHTHOL-YELLOW S.—Citronin A; Acid Yellow S.

$C_{10}H_4(NO_2)_2(OH)(SO_3Na)$ or $NaSO_3(\beta)C_6H_3C_4H(NO_2)_2.OH$.

Naphthol-yellow S is a monosulphonic acid of naphthol-yellow (or dinitronaphthol) in the form of the sodium salt. For its production alphanaphthol is converted into naphtholtrisulphonic acid by dissolving in fuming sulphuric acid, and to the solution nitric acid is added which transforms the trisulphonic acid into dinitroalphanaphthol monosulphonic acid.

Light-yellow or orange-yellow powder; aqueous solution, yellow; HCl makes the colour of the solution lighter without producing a precipitate; NaOH, no change; solution in H_2SO_4 , yellow; on diluting, the solution becomes lighter without yielding a precipitate. The potassium salt of naphthol-yellow S is sparingly soluble in water, and even very diluted solutions of the dyestuff are precipitated by caustic potash. The salt burns with scintillations on being heated on platinum.

Naphthol-yellow S may be adulterated with the cheaper naphthol-yellow. The latter can be detected by adding hydrochloric acid to the aqueous solution; naphthol-yellow is precipitated or the solution becomes milky, whereas a solution of pure naphthol-yellow S remains clear. If the dry colour is treated with ether, naphthol-yellow S will not colour the same alone or on addition of soda, while the ether is coloured yellow by naphthol-yellow and remains yellow on addition of soda.

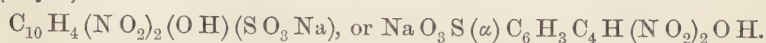
Application.—Wool is dyed at the boil in an acid bath with the addition of 5 per cent. of sodium bisulphate or $2\frac{1}{2}$ per cent. of sulphuric acid. Add the colour solution and then the acid in very small portions; work half an hour, wash and dry.

Silk is dyed in a boiled-off liquor bath to which sufficient sulphuric acid has been added to produce an acid reaction. Add the colour solution, raise the temperature to the boiling point, work 25 to 30 minutes, wash, brighten, and dry.

Naphthol-yellow S gives shades which are of a purer yellow than those of naphthol-yellow, slightly faster to light and fairly fast to milling. It is not volatile and does not evaporate from the fibre at a temperature below 120° . Hence it is suitable for the printing of woollen and silk fabrics.

Naphthol-yellow S mixes well with all acid colours. Picric acid has been almost completely replaced by this dyestuff.

BRILLIANT-YELLOW (Schoellkopff). **NAPHTHOL-YELLOW R S** (Bayer).



This colouring matter is also a monosulphonate of naphthol-yellow and is prepared by the action of nitric acid on a solution of alpha-naphthol disulphonic acid (Sch.) in diluted sulphuric acid.

Light-yellow powder; on being heated it swells up, but does not explode; aqueous solution, brownish-yellow; H Cl , light-yellow; Na O H , orange-yellow precipitate, soluble on heating; solution in $\text{H}_2\text{S O}_4$, pale-yellow; on diluting, light-yellow.

Application and Properties.—Same as naphthol-yellow S. It dyes a more reddish shade of yellow.



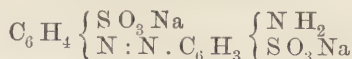
Aurantia is the sodium compound of *hexanitrodiphenylamine* prepared by the action of fuming nitric acid on diphenylamine dissolved in sulphuric acid.

Orange-yellow to red-brown powder or crystals; aqueous solution, orange-yellow; H Cl , light-yellow precipitate of hexanitrodiphenylamine (melting at 238°); Na O H , intensely orange colour; solution in $\text{H}_2\text{S O}_4$, pale-yellow; on diluting, yellow precipitate.

Application.—Aurantia has been used for the dyeing of wool and silk which it dyes orange in acid baths. It has been almost completely replaced by the azo-colours and is only used in the dyeing of leather. It possesses little fastness to the various agents.

AZO-COMPOUNDS.

FAST YELLOW G, or ACID YELLOW G.



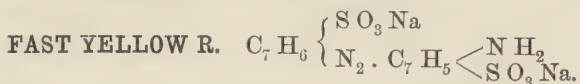
Fast yellow is the *sodium disulphonate of amidoazobenzene*, containing varying quantities of the monosulphonate; it is produced by the action of fuming sulphuric acid on amidoazobenzene (a yellow colouring matter).

Yellow powder; aqueous solution, yellow; H Cl , red-orange; Na O H , causes no change; solution in $\text{H}_2\text{S O}_4$, brownish-yellow; on diluting, red.

Application.—Wool is dyed with the addition of 5 per cent. of sodium bisulphate, or $2\frac{1}{2}$ per cent. of sulphuric acid to the bath. Heat the bath to the boiling point, add the colour solution, work for half an hour, wash, and dry. Excess of acid reddens the shade.

Fast yellow G dyes a shade similar to flavin, which is fairly fast to light and milling. It is as fast to light as the best natural yellow colouring matters, but it is not very brilliant, and is sensitive to acids. The dyestuff is suitable for the dyeing of compound shades, since it is taken up evenly by the wool fibre.

Silk is dyed with fast yellow in a boiled-off liquor bath, slightly acidulated with sulphuric acid. It can also be dyed without boiled-off liquor in a bath acidified with acetic acid. Add the colour gradually, work the yarn at the boil for half an hour, rinse, brighten with acetic or sulphuric acid, wash, and dry.



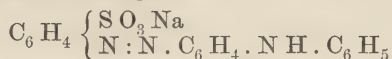
Fast yellow R is produced analogously to fast yellow G, by sulphonating amidoazotoluene.

Brown-yellow powder; aqueous solution, yellow; HCl, crimson; NaOH, no change; solution in H_2SO_4 , yellowish-brown; on diluting, magenta-red.

Application and Properties.—Same as fast yellow G. The shade is more orange-yellow.

DIPHENYLAMINE-ORANGE.

Orange IV. Orange N, or M, or G S, New Yellow, Acid Yellow D, Diphenyl-Orange.



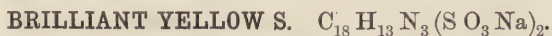
Diphenylamine-orange is produced by combining diazotised sulphanilic acid with diphenylamine, and converting the product into the sodium-salt.

Orange-yellow powder or tablets, not readily soluble in water; aqueous solution, orange-yellow; HCl, grey precipitate and red-violet solution; NaOH, soluble light-yellow precipitate; solution in H_2SO_4 , blue-violet; on diluting, purplish precipitate.

Application.—Same as fast yellow G.

Diphenylamine-orange has great tinctorial power. It dyes a yellowish-orange shade, which is fairly fast to milling, and moderately fast to light. Acids turn the shade blue-violet.

This dyestuff is extensively used, especially for shading purposes, on wool and on silk.



This product is a sulphonated diphenylamine-orange, and is produced by the action of sulphuric acid on that colouring matter.

Orange-yellow powder; aqueous solution, yellow; HCl, violet-red; NaOH, no change or violet-red solution; solution in H_2SO_4 , bluish red; on diluting, crimson.

Application.—Same as fast yellow G.

It dyes a redder and more brilliant shade of yellow than fast yellow, but less red than diphenylamine-orange.

AZO-FLAVIN (NEW YELLOW).

Indian Yellow, Azo-Yellow, Acid Azo-Yellow, Curcumein, Citronin.

The dyestuffs which are sold under this great variety of names are not of a uniform composition. They are produced by the action of nitric acid on mixtures of diphenylamine-orange and diphenylamine, and consist of more or less nitrated derivatives of these substances.

The dyestuffs were invented and first introduced into commerce under the name of *new yellow* by the firm of Tillmanns, E. Ter Meer & Co.

The commercial products are also different in solubility; some dissolve readily, whereas others do not yield a clear solution. They show the following reactions:—Ochre-yellow powder; aqueous solution, yellow; H Cl, dark red-brown or crimson precipitate or solution; Na O H, soluble brownish precipitate; solution in H₂ S O₄, violet; on diluting, brownish colour or precipitate.

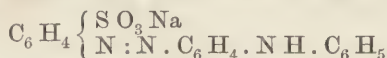
Application.—Same as naphthol-yellow S.

The different products produce a greenish-yellow, which is superior in beauty to almost all other acid yellows. It does not fade, becoming darker on exposure to light, is fairly fast to milling, and not sensitive to dilute acids.

Azo-flavin is extensively used in wool and silk dyeing, especially for shading purposes, and is employed in the printing of wool and silk.

METANIL-YELLOW.

Tropaeolin G, Orange M N, Victoria-Yellow.



(Azo-compound of metanilic acid and diphenylamine.)

Brownish-yellow powder; aqueous solution, orange-yellow; H Cl, purplish solution and dark flocculent precipitate; Na O H, no change; solution in H₂ S O₄, violet; on diluting, purplish.

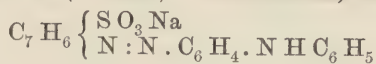
Application.—Same as fast-yellow G. The shade is redder and more brilliant than that of fast yellow. It is rather sensitive to acids, and, in dyeing, not too much acid should be used; an excess of sulphuric acid may be neutralised, however, by the addition of sodium acetate to the bath.

The shade is fairly fast to light and milling. Metanil-yellow is principally used in wool dyeing as a self-colour. Its sensitiveness to acids prevents the general use of the colouring matter for shading and for silk dyeing.

METANIL-YELLOW S (Oehler).

This is probably a sulphonate of metanil-yellow. It shows the same reaction as metanil-yellow, except that caustic soda produces a soluble yellow precipitate in the aqueous solution.

Application.—Same as fast yellow G. The shade is less reddish than that of metanil-yellow and less sensitive to acids. It is fairly fast to light and milling.

JAUNE SOLIDE N (Poirrier). **Curcumeïn, Orange N.**

(Azo-compound of paratoluidine orthosulphonic acid and diphenylamine).

Yellow-red powder; aqueous solution, yellow; HCl, steel-blue precipitate; solution in H_2SO_4 , blue-green; on diluting, steel-blue precipitate.

Application.—Same as fast yellow G. Jaune solide N yields a reddish-yellow or orange shade similar to metanil-yellow, and is fairly fast to light and milling.

METHYL-ORANGE.

Helianthin. Tropaeolin D, Orange III. or No. 3, Dimethylaniline-Orange, Golden Orange.

Sulphanilic acid—dimethylaniline.

Orange-yellow crystalline powder; aqueous solution, golden yellow; HCl, red-brown precipitate and red solution; NaOH, soluble yellow precipitate; solution in H_2SO_4 , brownish-yellow; on diluting, crimson.

Methyl-orange is very sensitive towards the action of strong acids by which the solution is turned red; it is used on this account as an indicator in volumetric analysis.

Application.—Same as fast yellow G.

Methyl-orange dyes a fine yellowish-orange, which, however, possesses little fastness to light and milling and is extremely sensitive to acids. This last property limits its employment in dyeing.

CHRYSOÏN or **TROPAEOLIN R.**

Resorcin - yellow, Tropaeolin O, Golden Yellow, Akmé-Yellow, Yellow T, Chryseolin.

Sulphanilic acid—resorcin.

Brown powder; aqueous solution, orange-yellow; HCl, no change; NaOH, red-orange; solution in H_2SO_4 , yellow; on diluting, orange-yellow.

Application.—Same as fast yellow G. The shade is slightly redder than fast yellow G; chrysoïn is nearly fast to light and milling; it is not affected by acids, but is turned into a brownish-red by alkalis.

Chrysoïn dyes very evenly ; it is principally used for compound shades in the dyeing of wool and silk.

It is one of the fastest of these dyestuffs, but a rather expensive article.

ALPHNAPHTHOL-ORANGE.

Orange I. or No. 1, Tropaeolin 000 No. 1.

Sulphanilic acid—alphanaphthol.

Red-brown powder ; aqueous solution, orange-red ; H Cl , brown precipitate ; Na O H , cherry-red ; solution in $\text{H}_2\text{S O}_4$, red-violet ; on diluting, orange.

Application.—Same as fast yellow G.

Alphanaphthol-orange dyes a red-orange shade, and is principally used in wool dyeing for bottoming being subsequently topped with other dyestuffs. It possesses considerable tinctorial power.

Alphanaphthol-orange is fairly fast to light ; not quite so fast to milling and rubbing.

BETANAPHTHOL-ORANGE or ORANGE II. (or No. 2).

Tropaeolin 000 No. 2, Mandarin G extra, Golden Orange, Orange extra, Chrysaurein, &c.

Sulphanilic acid—betanaphthol.

Yellowish-red powder ; aqueous solution, orange-yellow ; H Cl , dark orange precipitate ; Na O H , brown-red ; solution in $\text{H}_2\text{S O}_4$, crimson-red ; on diluting, brown-yellow precipitate.

Application.—Wool and Silk are dyed with betanaphthol-orange in the same way as with fast yellow G.

Betanaphthol-orange dyes a reddish shade of orange, a little less reddish than alphanaphthol-orange. It possesses the same fastness to light, milling, and rubbing as alphanaphthol-orange, and is not sensitive either to acids or alkalies.

Betanaphthol-orange is very extensively employed in wool dyeing, both as a self-colour and in combination with indigo-carmin, acid magenta, and other acid colours to produce mode colours.

Cotton can also be dyed with betanaphthol-orange ; the shade is moderately fast to light but not to washing. The methods indicated in the beginning of this chapter (p. 505) are employed.

Narceïn is a compound of betanaphthol-orange with sodium bisulphite which has been used in calico-printing. It is decomposed by steaming, betanaphthol-orange being liberated.

ORANGE T or R. Mandarin G R, Kermesin-Orange.

Orthotoluidinemonosulphonic acid—betanaphthol.

Brick-red powder ; aqueous solution, reddish-orange ; H Cl , gelatinous yellowish-brown precipitate ; Na O H , soluble brownish-orange precipitate ; solution in $\text{H}_2\text{S O}_4$, crimson ; on diluting, yellowish-brown precipitate.

Application.—Same as fast yellow G. The dyestuff strongly resembles betanaphthol-orange and can also be fixed like this on cotton. It is slightly redder in shade.

ORANGE R or 2 R.

Xylidinemonosulphonic acid—betanaphthol.

Fiery-red powder; aqueous solution, orange-yellow; H Cl, brown-red precipitate; Na O H, brown-yellow; solution in H_2SO_4 , cherry-red; on diluting, brown-red precipitate.

Application and Properties.—Same as betanaphthol-orange; the shade is redder.

ORANGE G or 2 G.

Aniline—betanaphthol disulphonic acid (G salt).

Orange-red powder; aqueous solution, orange-yellow; H Cl, no change; Na O H, yellow-red; solution in H_2SO_4 , orange-yellow; on diluting, no change.

Application.—Same as fast yellow G.

Orange G dyes a yellow shade of orange, which is fairly fast to light and milling, faster than most of the other acid azo-colours, and is not sensitive to acids or alkalis. It dyes very evenly, and is principally used for the production of compound shades in wool dyeing.

CROCEÏN-ORANGE. Ponceau 4 G B. Brilliant Orange G.

Aniline—betanaphthol monosulphonic acid S.

Fiery-red powder; aqueous solution, orange-yellow; H Cl, orange precipitate; Na O H, no change; solution in H_2SO_4 , orange-yellow; on diluting, brownish-yellow precipitate.

Application.—Same as fast yellow G.

Croceïn-orange dyes a redder shade of orange than the preceding dyestuff, and possesses greater tinctorial power. The shade is fairly fast to light and milling, and not sensitive to dilute acids and alkalis.

Croceïn-orange dyes very evenly, and is used extensively by colour-makers and drysalers for mixing of wool colours; it is also employed for the production of lakes.

ORANGE G T or R N.

Toluidine—betanaphthol monosulphonic acid.

Scarlet-red powder; aqueous solution, orange-yellow; H Cl, brownish oil; Na O H, dark brown-red solution; solution in H_2SO_4 , magenta-red; on diluting, brownish oil.

Application.—Same as fast yellow G. This dyestuff resembles croceïn-orange.

BRILLIANT ORANGE R. SCARLET R or G R.

Xylidine—betanaphthol monosulphonic acid S.

Vermilion-red powder; aqueous solution, reddish-orange; H Cl,

brown-red precipitate; NaOH , no change; solution in H_2SO_4 , cherry-red; on diluting, brown-red precipitate.

Application.—Same as fast yellow G. Brilliant orange R dyes a yellowish-scarlet or red-orange, redder than orange GT; it closely resembles this dyestuff.

DOUBLE BRILLIANT SCARLET G (Berlin). Orange-red I.

Betanaphthylamine sulphonic acid (Br.)—betanaphthol.

Red-brown powder; aqueous solution, yellowish-red; HCl , brown precipitate; NaOH , soluble red-brown precipitate; solution in H_2SO_4 , crimson; on diluting, brown-red precipitate.

Application and Properties.—Same as betanaphthol-orange.

Double brilliant scarlet G dyes a yellow-scarlet shade.

SCARLET 2 G.

Aniline—betanaphthol disulphonic acid (R salt).

Fiery-red powder; aqueous solution, reddish-orange; HCl , no change; NaOH , more yellowish; solution in H_2SO_4 , cherry-red; on diluting, reddish-orange.

Application and Properties.—Same as xylidine scarlets (see next page).

Scarlet 2 G dyes a reddish-orange; on prolonged exposure to light it becomes more yellowish.

ORANGE III. or No. 3. (Poirrier).

Metanitriline—betanaphthol disulphonic acid (R salt).

Red-brown powder; aqueous solution, reddish-yellow; HCl , soluble orange-yellow precipitate; NaOH , yellowish-brown; solution in H_2SO_4 , orange-yellow; on diluting, soluble orange-yellow precipitate.

Application.—Same as fast yellow G. Orange III. yields an orange shade, which is fairly fast to light, and resists milling very well.

SCARLET R T or R.

Toluidine—betanaphthol disulphonic acid (R salt).

Red powder; aqueous solution, yellowish-red; HCl , no change; NaOH , darker and more yellowish; solution in H_2SO_4 , cherry-red; on diluting, yellowish-red.

Application and Properties.—Same as xylidine-scarlets (see next page). The shade is more yellowish than scarlet 2 R.

SCARLET 2 R.

Metaxylidine—betanaphthol disulphonic acid (R salt).

Red powder; aqueous solution, yellowish-red; HCl , no change; NaOH , makes the solution darker and more yellowish; solution in H_2SO_4 , cherry-red; on diluting, more yellowish.

Application and Properties.—See next page, *Xylidine-scarlets*.

XYLIDINE-SCARLETS (SCARLET R, 2 R, and 3 R).

The scarlets (first introduced by the Farbwerke M. L. B.—Hoechst.) which are produced by the reaction of diazotised metaxylidine and the homologous and isomeric bases are known in commerce as xylidine-scarlets or scarlets R, 2 R, or 3 R. The commercial articles are not prepared from chemically pure substances and are mixtures of several very similar azo-compounds; they are produced by combining the more or less pure diazo-compounds of metaxylidine, pseudocumidine, and orthotoluidine with R salt. Scarlet 2 G (the analogous product from aniline) is also sometimes added for shading. Pure metaxylidine yields a shade like scarlet 2 R, and from pure pseudocumidine and R salt scarlet 4 R is obtained.

Scarlet G is a yellowish-scarlet, and is obtained as a bye-product in the manufacture of crystal-scarlet by the action of diazotised crude xylidine on a mixture of Schäffer's acid and R salt. It forms a brown-red powder and closely resembles the xylidine-scarlets.

The xylidine-scarlets evince the same tinctorial properties, and are not mixtures in the practical sense of the word; they behave exactly alike in the dye-bath, and are taken up by the fibre in equal proportions.

Application of the Xylidine-scarlets.—The xylidine-scarlets were the first azo-scarlets to be largely employed; they have rapidly replaced cochineal in the dye-house, owing to their low price and simple mode of application. They are less fast to light and to milling than cochineal, but in the fire and brilliancy of their shades they are quite equal to, if not superior to, cochineal.

The xylidine-scarlets are used in enormous quantities for wool dyeing; very extensively for silk dyeing (like the azo-colours generally) and to a limited extent for cotton dyeing; on this last-mentioned fibre, however, they cannot compete well with crocein-scarlet and similar products.

Cotton is dyed by the methods given in the beginning of this chapter (p. 505). The xylidine-scarlets do not form precipitates with alum, and do not require precautions in this respect.

Wool is dyed with xylidine-scarlets as with the other acid azo-colours. The wool is turned for a few-minutes in the boiling bath prepared with the colour solution only; then 5 to 10 per cent. of sodium bisulphate are gradually added in small portions, and the goods are worked at the boil until the bath is nearly exhausted, washed in water, and dried.

Goods which are difficult to dye through may be dyed with the addition of acetate of sodium or ammonium and acid to the bath. Add the colour solution and the acetate, turn some time, and then very gradually add sulphuric acid, sodium bisulphate, or preferably acetic acid in small portions; otherwise the dyeing proceeds as before.

The xylidine-scarlets are moderately fast to light; they resist milling fairly well and are fast to stoving.

Silk is dyed with the xylidine-scarlets in an acidified bath of boiled-off liquor and brightened with sulphuric acid. Acidulate the bath with sulphuric acid, add the colour solution, heat to the boil, and continue to boil for 25 to 30 minutes, rinse, brighten, and dry.

SCARLET 4 R.

Pseudocumidine—betanaphthol disulphonic acid (R salt).

For the production of this dyestuff purified pseudocumidine or *amido-trimethylbenzene* is used; whereas xylidine-scarlet 3 R is prepared with crude pseudocumidine. A similar dyestuff, which shows the same reactions and is known under the same name, is obtained from amido-dimethylethylbenzene.

Scarlet 4 R is a dark red powder; aqueous solution, red; H Cl, no change; Na OH, makes the solution more yellowish; solution in H_2SO_4 , crimson; on diluting, red.

Application and Properties.—Same as xylidine-scarlets. The shade is bluer than that of scarlet 3 R.

PALATIN-SCARLET A (B. A. S. F.)

This product is obtained by the action of diazotised xylidine on a disulphonic acid of naphthol, the constitution of which is not known.

Brown-red powder; aqueous solution, scarlet-red; H Cl, gelatinous yellow-brown precipitate; Na OH, more yellowish; solution in H_2SO_4 , bluish-red; on diluting, yellow-brown precipitate.

Application.—Same as xylidine-scarlets. Palatin-scarlet dyes a scarlet similar to xylidine-scarlet 2 R, which, however, possesses greater brilliancy and is almost fast to light (not inferior to cochineal in fastness to light). It is fairly fast to milling, and fast to stoving.

BIEBRICH SCARLET.

Scarlet B, Scarlet 3 R B, New Red L; Imperial Scarlet.

Amidoazobenzene sulphonic acid—betanaphthol.

Biebrich scarlet, introduced by Kalle & Co., was one of the first scarlets in the market. The commercial product is obtained from amidoazobenzene disulphonic acid, which contains some monosulphonic acid.

Fast Double Scarlet is produced from the pure monosulphonic acid of amidoazobenzene, and shows similar reactions and tinctorial properties.

Biebrich scarlet is a brown-red powder; aqueous solution, orange-red; H Cl, flocculent dark-red precipitate; Na OH, brown-red precipitate, soluble with a violet colour; solution in H_2SO_4 , green; on diluting, it turns from blue to red and yields a brown-red precipitate.

Biebrich scarlet forms an insoluble precipitate with alum in contrast with the isomeric compound crocein 3 B.

Application.—Same as xylidine-scarlets.

Biebrich scarlet dyes a bluish scarlet which has a brownish tint ; it dyes very level, and is suitable for mixed shades. The colour resembles the xylidine-scarlets as regards fastness to milling, acids, and alkalies, and is slightly faster to light.

Cotton is dyed by the methods indicated in the beginning of this chapter (p. 505). The material should be washed in water after the mordanting with aluminium compounds, and the dye-bath should be slightly acidulated with acetic acid, to prevent the dyestuff from being precipitated by alumina in the dye-liquor.

CROCEÏN-SCARLET 3 B (Bayer), **SCARLET 4 R B** (Berlin).

Amidoazobenzene monosulphonic acid—

betanaphthol sulphonic acid (B).

Croceïn-scarlet was the third of the scarlets which appeared in the market about a quarter of a century ago, and almost revolutionised the dyeing of red and mixed shades on wool. Its shade is purer than those of the xylidine and Biebrich scarlets, and excelled only by the *brilliant croceïns*.

Red-brown powder ; aqueous solution, scarlet-red ; H Cl, flocculent yellowish-brown precipitate ; Na OH, soluble dirty-violet-red precipitate ; solution in H_2SO_4 , blue ; on diluting, the solution passes through violet to red and forms a dark red precipitate.

Application.—Same as xylidine-scarlets. Union goods are dyed with 10 per cent. of alum, $2\frac{1}{2}$ per cent. of acetic acid, and 40 per cent. of common salt.

Croceïn-scarlet is slightly faster to washing on cotton than the xylidine-scarlets. Although greatly inferior to the direct cotton colours in fastness to washing, and supplanted by them to a great extent, it is still used in great quantities for the Eastern trade, where fastness to light is required.

On wool croceïn-scarlet dyes a very bright scarlet, which is superior to xylidine-scarlet in fastness to light and in brilliancy ; it is fairly fast to light and milling, but not fast to stoving in contrast with the xylidine-scarlets.

Croceïn-Scarlet R, B and 2 B are mixtures of croceïn-scarlet 3 B with the oranges.

Croceïn-Scarlet 5 B is a mixture of the croceïn-scarlets 3 B and 7 B.

CROCEÏN-SCARLET 7 B (Bayer). **PONCEAU 6 R B** (Berlin).

Amidoazotoluene monosulphonic acid—

betanaphthol sulphonic acid (B.)

Dull red powder ; aqueous solution, scarlet-red ; H Cl, little change, but the solution slowly becomes turbid ; Na OH, soluble dirty-violet precipitate ; solution in H_2SO_4 , blue ; on diluting, violet-red.

Application and Properties.—Same as crocein-scarlet 3 B. The shade is bluer; a pure bright red, almost crimson-red. It is suitable for compound shades in place of acid magenta.

BRILLIANT CROCEIN (Cassella). **COTTON-SCARLET** (M.L.B.; B.A.S.F.)

Amidoazobenzene—betanaphthol disulphonic acid (gamma acid).

Light brown powder; aqueous solution, cherry-red; H Cl, brown precipitate; Na O H, brown; solution in $H_2S O_4$, red-violet; on diluting, blue, then red solution and formation of a brownish precipitate.

Application.—Same as xylidine-scarlets and crocein-scarlets. Brilliant crocein is very similar to crocein-scarlet in fastness and possesses a purer shade; it is the finest of all the scarlets, and is used extensively for the dyeing of cotton, silk, wool, and other fibres. It dyes a shade similar to xylidine-scarlet 3 R and crocein-scarlet 3 B.

CROCEIN-SCARLET 3 B X (Bayer).

Naphthionic acid—betanaphthol monosulphonic acid (B).

Scarlet-red powder; aqueous solution, yellowish-red; H Cl, no change; Na O H, yellowish-brown; solution in $H_2S O_4$, red-violet; on diluting, yellowish-red.

Application.—Same as xylidine-scarlets. Crocein 3 B X resembles crocein 3 B in the appearance and fastness of shade; on cotton, however, it is not faster to washing than the xylidine-scarlets.

BRILLIANT SCARLET (4 R). COCHINEAL RED A. NEW COCCIN.

Naphthionic acid—betanaphthol disulphonic acid (gamma acid).

Scarlet-red powder; aqueous solution, scarlet-red; H Cl, no change; Na O H, dark orange; solution in $H_2S O_4$, dirty-red-violet; on diluting, red.

Application.—Same as xylidine-scarlets. Brilliant scarlet 4 R resembles crocein 3 B X; but it is slightly more brilliant.

CRYSTAL SCARLET (6 R). NEW COCCIN R.

Alphanaphthylamine—betanaphthol disulphonic acid (gamma acid).

Dark red crystals with a golden lustre; aqueous solution, red; H Cl, slightly darker; Na O H, more yellowish; solution in $H_2S O_4$, blue; on diluting, red.

Application.—Same as xylidine-scarlets. Crystal scarlet also resembles crocein 3 B X, but is more brilliant; the shade is bluer than that of crocein 3 B X and of brilliant scarlet 4 R.

AZO-COCCIN 2 R.

Xylidine—alphanaphthol sulphonic acid N W.

Red-brown powder, not freely soluble in water; aqueous solution, red; HCl , red-brown precipitate; NaOH , brownish-yellow; solution in H_2SO_4 , magenta-red; on diluting, brown-red precipitate.

Application.—Same as xyloidine-scarlets.

Azo-coccin 2 R yields shades which are similar to xyloidine-scarlet 2 R and 3 R, but less pure; it is faster to light, but less fast to milling than these dyestuffs; it is not sensitive to acids or alkalis. In dyeing, care must be taken that the dyestuff is not precipitated by alum in the dye-liquor.

AZO-EOSIN (Bayer).

Orthoanisidine—alphanaphthol sulphonic acid N W.

Red-orange powder; aqueous solution, red; HCl , brownish-orange precipitate; NaOH , brownish-orange; solution in H_2SO_4 , crimson-red; on diluting, brownish-orange precipitate.

Application.—Same as xyloidine-scarlets.

Azo-eosin yields a scarlet shade on wool—slightly bluer than crocein 3 B.

DOUBLE BRILLIANT SCARLET 3 R or EXTRA S (BRILLIANT SCARLET).

Betanaphthylamine sulphonic acid (Br)—

alphanaphthol sulphonic acid N W.

Brown-red powder; aqueous solution, yellowish-red; HCl , yellowish-brown flocculent precipitate; NaOH , no change; solution in H_2SO_4 , crimson; on diluting, yellowish-red.

Application.—Same as xyloidine-scarlets.

Double brilliant scarlet dyes a very pure and brilliant scarlet on wool.

PYROTIN R R O (Dahl).

Betanaphthylamine sulphonic acid (D)—

alphanaphthol sulphonic acid N W.

Brown-red powder; aqueous solution, yellowish-red; HCl , more bluish; NaOH , more yellowish; solution in H_2SO_4 , magenta-red; on diluting, red.

Application.—Same as xyloidine-scarlets.

Pyrotin R R O is used in cotton and wool dyeing for the production of scarlet shades.

SCARLET S EXTRA or FAST SCARLET 2 B.

Amidoazobenzene disulphonic acid—

betanaphthol disulphonic acid (R salt).

Brown powder; aqueous solution, magenta-red; HCl , little change; NaOH , soluble violet precipitate; solution in H_2SO_4 , blue; on diluting, yellowish.

Application.—Same as xyloidine-scarlets. Scarlet S extra dyes a bluish shade of scarlet, which is equal to the xyloidine-scarlets in fastness to light and to milling. It dyes slowly and evenly, and is very suitable for goods difficult to dye through.

SCARLET 2 S EXTRA.

Amidoazobenzene—betanaphthol disulphonic acid (R salt).

Brown powder; aqueous solution, magenta-red; H Cl, violet precipitate; Na OH, violet; solution in H_2SO_4 , violet; on diluting, violet precipitate.

Application.—Same as xyloidine-scarlets.

Scarlet 2 S extra is similar to scarlet S extra; it dyes a slightly bluer shade.

SCARLET 5 R (M. L. B.) ERYTHRIN X (B. A. S. F.)

Amidoazobenzene—betanaphthol trisulphonic acid.

Brown powder; aqueous solution, cherry-red; H Cl, violet precipitate; Na OH, violet; solution in H_2SO_4 , blue-violet; on diluting, red.

Application.—Same as xyloidine-scarlets.

Scarlet 5 R dyes a bluish shade of scarlet on wool, which possesses great fastness to light.

SCARLET 6 R (M. L. B.; B. A. S. F.)

Naphthionic acid—betanaphthol trisulphonic acid.

Brown powder; aqueous solution, cherry-red; H Cl, no change; Na OH, red-brown; solution in H_2SO_4 , blue-violet; on diluting, magenta-red.

Application.—Same as xyloidine-scarlet.

Scarlet 6 R is similar to the preceding dyestuff. It produces an equally fast and still bluer scarlet on wool.

COCHINEAL-SCARLET G (Schoellkopf).

Aniline—alphanaphthol sulphonic acid (Cl).

Brick-red powder; aqueous solution, yellowish-red; H Cl, brown-red precipitate; Na OH, orange; solution in H_2SO_4 , cherry-red; on diluting, brown-red precipitate.

Application.—Cochineal-scarlet and the following dyestuffs of the same American firm are not used to our knowledge except in the United States. It seems that they cannot compete in price under equal conditions with the other scarlets, although they produce fine shades. The crocein-scarlets (Schoellkopf) possess some importance for cotton dyeing.

Cochineal-scarlet G is applied like the xyloidine-scarlets, but possesses greater fastness on cotton. The dyestuff forms insoluble precipitates with calcium and magnesium salts; hence calcareous water or—for cotton dyeing—salt containing much magnesium should be avoided

or purified. Cochineal-scarlet G and 2 R sometimes require a comparatively large quantity of acid for dyeing. Cochineal-scarlet G dyes a yellow shade of scarlet, which is fairly fast to light.

COCHINEAL-SCARLET 2 R (Schoellkopf).

Orthotoluidine—alphanaphthol sulphonic acid (Cl).

Vermilion-red powder; aqueous solution, yellowish-red; H Cl, red precipitate; Na O H, orange; solution in $H_2S O_4$, magenta-red; on diluting, red flocculent precipitate.

Application and Properties.—Same as the preceding dyestuff; the shade is a fiery scarlet.

CROCEÏN-SCARLET B and 3 B (Schoellkopf).

These two dyestuffs are obtained by the action of diazotised amidoazobenzene, or amidoazo-orthotoluene respectively, on alphanaphthol disulphonic acid (Sch). They show nearly the same reactions.

Red powder (scarlet B) or brown powder (scarlet 3 B); aqueous solution, bluish-red; H Cl, violet precipitate; Na O H, violet; solution in $H_2S O_4$, violet; on diluting, violet precipitate.

Application.—Same as xylidine-scarlets and croceïn-scarlets.

These two croceïn-scarlets are used to some extent in the United States for cotton dyeing. They produce on this fibre bluish-red shades, which are equal to the croceïn-scarlets (Bayer) in fastness to light and washing.

WOOL-SCARLET R (Schoellkopf).

Xylidine—alphanaphthol disulphonic acid (Sch).

Brown-red powder; aqueous solution, yellowish-red; H Cl, bluish-red; Na O H, red-orange; solution in $H_2S O_4$, cherry-red; on diluting, red.

Application.—Wool-scarlet R is dyed on wool in the same way as xylidine-scarlet and the other acid dyestuffs; it yields a fiery scarlet, which is fairly fast to light and to milling.

BUFFALO-RUBIN (Schoellkopf).

Alphanaphthylamine—alphanaphthol disulphonic acid (Sch).

Brown powder; aqueous solution, magenta-red; H Cl, no change; Na O H, no change; solution in $H_2S O_4$, blue; on diluting, magenta-red.

Application.—Buffalo-rubin is also dyed on wool in the same way as the acid colours generally. It dyes a claret-red shade, which is fairly fast to light and milling.

FAST RED or FAST RED A.

Roccellin, Rauracienne, Cerasin, Orcellin No. 4, Rubidin.

Naphthionic acid—betanaphthol.

Brown-red powder, not very soluble in cold water; aqueous solution,

red; HCl , yellowish-brown precipitate; NaOH , dark purplish-red; solution in H_2SO_4 , violet; on diluting, yellowish-brown precipitate.

Application.—Fast red A and the other “fast reds” may replace orchil in wool and silk dyeing. They can be dyed in the same way as the xylidine-scarlets on the various fibres. It is, however, more difficult to dye these colours evenly on wool, since they are too rapidly taken up by the fibre, the methods indicated below are more suitable for dyeing wool with the fast reds.

Cotton.—Fast red A forms a precipitate with alum; hence the material which has been mordanted with this substance must be washed in water before dyeing. The colour is not fast to washing.

Wool.—The dye-bath is prepared with the colour solution and about 10 per cent. of Glaubersalt; the wool is introduced at 40°C . and the bath heated to the boil after some minutes’ working; finally, 5 per cent. of sodium bisulphate are added very gradually while the boiling is continued; when the bath is exhausted, the goods are wrung out, washed, and dried. Satisfactory results are obtained in this way. The fourth, fifth, and sixth method, given in the introduction of this chapter are still better adapted, especially the fourth method (p. 507). Fast red A produces a beautiful pure red shade on wool, which, however, is only moderately fast to light and milling; it is not affected by dilute acids or alkalis.

Silk is dyed in an acidified bath of boiled-off liquor. Make the bath slightly acid with sulphuric acid, add the colour solution, turn the goods for 10 to 15 minutes in the warm bath, heat to the boil and work at this temperature for 20 to 25 minutes, rinse in water, brighten in sulphuric acid, wring, and dry.

FAST RED B. BORDEAUX B.

Alphanaphthylamine—betanaphthol disulphonic acid (R salt).

Brown powder; aqueous solution, claret-red; HCl , no change; NaOH , soluble red-brown precipitate; solution in H_2SO_4 , blue; on diluting, crimson.

Application and Properties.—Same as fast red A.

Fast red B dyes bluish claret-red shades, bluer and less pure than fast red A.

Nacarat S is said to be a mixture of fast red B and xylidine-scarlet (*Kertecz*).

FAST RED C. Azo-Rubin A or S, Carmoisin, Acid Azo-Rubin.

Naphthionic acid—alphanaphthol sulphonic acid (NW).

Red-brown powder; aqueous solution, crimson; HCl , dark red precipitate; NaOH , more yellowish; solution in H_2SO_4 , violet; on diluting, crimson.

Application.—Same as xylidine-scarlets (see page 519).

Fast red C produces red shades on wool intermediate between those

of fast red B and acid magenta ; it is used in the production of compound shades as a substitute for the latter dyestuff, since it is faster to light and milling and not sensitive to alkalies.

FAST RED D. AMARANTH.

Bordeaux S, Acid azo-rubin 2 B, Victoria-rubin.

Naphthionic acid—betanaphthol disulphonic acid (R salt).

Red-brown powder ; aqueous solution, crimson ; H Cl, no change ; Na O H, darker ; solution in H_2SO_4 , violet ; on diluting, crimson.

Application.—Same as xyloidine-scarlets.

Fast red D dyes a pure bluish-red shade, which comes near to the claret-reds or "bordeaux." It is fairly fast to light and to milling, and has the advantage over fast red A that it dyes evenly without difficulty.

FAST RED E.

Naphthionic acid—betanaphthol sulphonic acid (S).

Red-brown powder ; aqueous solution, claret-red ; H Cl, darker ; Na O H, brownish-red ; solution in H_2SO_4 , violet ; on diluting, red.

Application and Properties.—Same as fast red A. The shade is similar to fast red A. The colour goes rather more evenly on to the fibre.

FAST RED B T.

Alphanaphthylamine—betanaphthol sulphonic acid (S).

Red powder ; aqueous solution, red ; H Cl, dark red-brown precipitate ; Na O H, brown ; solution in H_2SO_4 , dark violet ; on diluting, dark brown-red precipitate.

Application and Properties.—Same as fast red A.

Fast red B T dyes a medium shade of claret-red on wool.

PALATIN-RED (B. A. S. F.)

Alphanaphthylamine—naphthol disulphonic acid.

This naphthol disulphonic acid, the constitution of which has not yet been described, is identical with that of palatin-scarlet A. (See *Palatin-scarlet A*, p. 520).

Brown powder ; aqueous solution, red ; H Cl, little change ; Na O H, red-brown ; solution in H_2SO_4 , blue ; on diluting, red.

Application.—Same as xyloidine-scarlets.

Palatin-red dyes a very bright and pure bluish shade of red, even finer than fast red D. It is fairly fast to light, milling, and stoving.

OENANTHININ (Durand).

Naphthionic acid—naphthol disulphonic acid.

Red-brown powder ; aqueous solution, crimson ; H Cl, no change ; Na O H, more yellowish ; solution in H_2SO_4 , violet ; on diluting, crimson.

Application.—Oenanthinin dyes a full bluish-red shade in an acid bath; it serves as an orchil substitute in wool and silk dyeing.

ROXAMIN (Durand).

Naphthionic acid—(2 : 7) dioxynaphthalene.

Brick-red powder; aqueous solution, scarlet; HCl , no change; NaOH , darkens the solution; solution in H_2SO_4 , intense violet; on diluting, no change.

Application.—Roxamin is also used as a substitute for orchil in wool and silk dyeing, and is dyed like fast red A. It dyes a pure red shade.

BORDEAUX G (Bayer).

Amidoazotoluene monosulphonic acid—

betanaphthol sulphonic acid (S).

Brown-red powder; aqueous solution, red; HCl , red precipitate; NaOH , violet; solution in H_2SO_4 , dark blue; on diluting, red precipitate.

Application.—Same as fast red A.

Bordeaux G produces a yellowish shade of claret-red on wool.

BORDEAUX B X (Bayer).

Amidoazoxylene—betanaphthol disulphonic acid (S).

Brown powder; aqueous solution, brown-red; HCl , brown-red precipitate; NaOH , soluble brown-red precipitate; solution in H_2SO_4 , green; on diluting, brown-red precipitate.

Another *Bordeaux B X* (Bayer) is prepared from amidoazoxylene disulphonic acid and betanaphthol. The reactions of both compounds are similar.

Application.—Same as fast red A.

Bordeaux B X dyes on wool bluish shades of claret-red.

ORCHIL SUBSTITUTE G (Berlin).

Paranitraniline—betanaphthol sulphonic acid (Br).

Red-brown powder; aqueous solution, HCl , slimy brown precipitate; NaOH , brownish-red fine precipitate; solution in H_2SO_4 , red; on diluting, slimy brown precipitate.

Application.—Orchil substitute G and the following dyestuffs are intended, as indicated by their names, as substitutes for orchil, and produce shades similar to those obtained with orchil in an acid bath. They are employed in large quantities in wool dyeing, and are dyed in the same way as the acid colours, and as fast red A especially. The shades are fairly fast to light, but less fast to milling; they are, however, better in this respect than those produced with orchil.

ORCHIL SUBSTITUTE V (Poirrier, Berlin). *Naphthion red.*

Paranitraniline—naphthionic acid.

Brown paste ; aqueous solution, red-brown ; H Cl, brown-red precipitate ; Na O H, soluble brown-red precipitate ; solution in H_2SO_4 , crimson ; on diluting, brown-red precipitate.

Application.—Same as orchil substitute G.

ORCHIL SUBSTITUTE V N (Poirrier, Berlin).

Paranitraniline—alphanaphthylamine sulphonic acid (L).

Dark-brown powder ; aqueous solution, red ; H Cl, more bluish ; Na O H, brownish ; solution in H_2SO_4 , red ; on diluting, little change.

Application.—Same as orchil substitute G.

ORCHIL SUBSTITUTE EXTRA (Cassella). **APOLLO-RED** (Geigy).

Paranitraniline—alphanaphthylamine disulphonic acid.

Brown powder ; aqueous solution, brown-red ; H Cl, crimson ; Na O H, soluble brown precipitate ; solution in H_2SO_4 , crimson ; on diluting, no change.

Application.—Same as orchil substitute G.

ORSEILLIN 2 B (Bayer).

Amidoazotoluene monosulphonic acid—

alphanaphthol sulphonic acid (N W).

Brown powder ; aqueous solution, crimson ; H Cl, red-violet ; Na O H, more yellowish ; solution in H_2SO_4 , blue ; on diluting, crimson.

Application.—Same as orchil substitute G.

ORCHIL-RED A (B. A. S. F.)

Amidoazoxylenes—betanaphthol disulphonic acid (R salt).

Dark-brown powder ; aqueous solution, dark bluish-red ; H Cl, brown-red precipitate ; Na O H, soluble brown-red precipitate ; solution in H_2SO_4 , dark blue ; on diluting, crimson.

Application.—Same as orchil substitute G. Orchil-red A dyes on wool in an acid bath a valuable shade of bluish-red, which is distinguished by great fastness to light.

The dyestuff can also be dyed (like the cloth-reds) on wool which has been previously mordanted with chromium, and thus yields more brownish shades, which resemble the cloth-reds in fastness to milling (see under *Mordant Colours*).

AZO-FUCHSIN G (Bayer).

Sulphanilic acid—dioxynaphthylene alphasulphonic acid (1 : 8).

Red-brown powder ; aqueous solution, bluish-red ; H Cl, more yellowish ; Na O H, more bluish ; solution in H_2SO_4 , violet ; on diluting, bluish-red.

Application.—See *Azo-fuchsin B*.

AZO-FUCHSIN B (Bayer).

Toluidine—dioxynaphthalene alphasulphonic acid (1 : 8).

Black-brown powder; aqueous solution, bluish-red; H Cl, red-brown precipitate; Na O H, more bluish; solution in H_2SO_4 , violet; on diluting, bluish-red.

Application.—Azo-fuchsin G and B are two recent additions to the list of valuable dyestuffs. Like the other acid colours they are dyed on wool with the addition of sodium bisulphate and on silk in an acidulated soap-bath. Azo-fuchsin G dyes very even, and the brand B fairly well; the former is especially suitable for compound shades in place of acid magenta. They dye bluish-red shades (magenta-red), azo-fuchsin B being bluer than the other. The shades are fairly fast to light, milling, and stoving, acids and alkalies, and are better in this respect than most of the orchil substitutes.

FAST VIOLET, REDDISH (Bayer).

Sulphanilic acid—azonaphthylamine—betanaphthol sulphonic acid (S).

For the production of this dyestuff sulphanilic acid is diazotised and combined with alphanaphthylamine; the product is rediazotised and combined with alphanaphthol sulphonic acid (S).

Dark powder with a green metallic reflex; aqueous solution, red-violet; H Cl, red-violet precipitate; Na O H, soluble red-violet precipitate; solution in H_2SO_4 , dark bluish-green; on diluting, red-violet precipitate.

Application.—Fast violet dyes in an acid bath dull reddish-violet to violet-black shades on wool, which are fairly fast to light and to milling; it is applied in the same way as the other acid colours. On wool which has been mordanted with chromium oxide fast violet produces dark shades which are fast to milling.

FAST VIOLET, BLUISH (Bayer).

Paratoluidine sulphonic acid—azonaphthylamine—
betanaphthol sulphonic acid (S).

This colouring matter is produced analogously with the preceding one.

Dark brown powder; aqueous solution, violet; H Cl, violet precipitate; Na O H, soluble violet precipitate; solution in H_2SO_4 , dark green; on diluting, violet precipitate.

Application and Properties.—Same as fast violet, reddish. The shade is a dull violet.

FAST BROWN (M. L. B.)

Xylidine sulphonic acid > alphanaphthol.
Xylidine sulphonic acid

Dark brown powder; aqueous solution, brown; H Cl, violet precipitate; Na O H, reddish-yellow; solution in H_2SO_4 , violet; on diluting, red.

Application.—Fast brown is dyed on wool and silk in the same way as the other acid colours. As it is liable to dye uneven, the dyeing of wool should be started at about 40° in a neutral bath, and sodium bisulphate be added very gradually in small portions. Fast brown produces a moderately fast brown-red shade, which is not very brilliant.

NAPHTHYLAMINE-BROWN or FAST BROWN N (B. A. S. F.)

Naphthionic acid—alphanaphthol.

Dark brown powder; aqueous solution, yellowish-brown; H Cl, dark brown precipitate; Na O H, red-brown; solution in H_2SO_4 , blue; on diluting, brown precipitate.

Application.—Same as fast brown.

Naphthylamine-brown dyes an orange-brown, which lacks brilliancy and brightness, and is not fast to milling, but fairly fast to light.

FAST BROWN (Bayer).

Naphthionic acid > resorcin.
Naphthionic acid >

This dyestuff is similar to the two preceding.

FAST BROWN G (Berlin).

Sulphanilic acid > alphanaphthol.
Sulphanilic acid >

Brown powder; aqueous solution, red-brown; H Cl, soluble violet precipitate; Na O H, cherry-red; solution in H_2SO_4 , violet; on diluting, yellowish-brown.

Application.—Fast brown G resembles also the preceding brown dyestuffs, and is applied in the same way. It yields yellowish-brown shades.

FAST BROWN 3 B (Berlin).

Betanaphthylamine sulphonic acid (Br)—alphanaphthol.

Brown powder; aqueous solution, brown-red; H Cl, red-violet; Na O H, crimson; solution in H_2SO_4 , blue; on diluting, red-violet precipitate.

Application.—Fast brown 3 B is also similar to the preceding fast browns, and is applied in the same way. It dyes reddish-brown shades.

ACID BROWN G (Berlin).

Aniline—chrysoïdine monosulphonic acid.

Brown powder; aqueous solution, brown; H Cl, no change; Na O H, no change; solution in H_2SO_4 , red-brown; on diluting, yellowish-brown.

Similar, but redder in shade is:

ACID BROWN R (Berlin).

Naphthionic acid—chrysoïdine.

Brown powder ; aqueous solution, brown ; H Cl, brown precipitate ; Na OH, no change ; solution in H_2SO_4 , dark olive ; on diluting, brown precipitate.

ORCELLIN (Leonhardt).

Composition not known.

Dark brown powder ; aqueous solution, claret-red ; H Cl, little change ; Na OH, more bluish ; solution in H_2SO_4 , dark violet ; on diluting, red.

Application.—Wool is dyed with this dyestuff in an acid bath a dark reddish-brown, which resists hot soaping and light fairly well, and is moderately fast to milling. It can also be dyed on chromium mordants.

Silk is dyed in a boiled-off liquor bath acidulated with sulphuric acid. Enter at about 30° , heat slowly to the boiling point, and boil for some time. Violet-brown shades, fairly fast to light and washing, are obtained.

RESORCIN-BROWN (Berlin).

Xylidine—chrysoin.

This dyestuff is obtained by the action of diazotised xylidine on the orange-yellow dyestuff chrysoin or tropaeolin R (*sulphanilic acid azo-resorcin*) (p. 515).

Brown powder ; aqueous solution, yellowish-brown ; H Cl, soluble brown precipitate ; Na OH, more reddish ; solution in H_2SO_4 , reddish-brown ; aqueous solution, brown precipitate.

Application.—Resorcin-brown is dyed by the ordinary methods used for the acid colours—*e.g.*, the xylidine-scarlets. It dyes a fine yellowish-brown shade, which is fairly fast to light and milling on wool.

NAPHTHOL-BLACK B (Cassella). **BRILLIANT-BLACK** (B. A. S. F.)

Amidoazonaphthalene disulphonic acid—

betanaphthol disulphonic acid (R salt).

For the production of naphthol-black B amidoazonaphthalene disulphonic acid is prepared by the action of diazotised betanaphthylamine gammadisulphonic acid on alphanaphthylamine ; this compound is rediazotised, and combined with betanaphthol disulphonic acid (R salt).

Similar products are :—

Naphthol-black 3 B and **6 B** (Cassella).—They are produced in the same way, the betanaphthylamine disulphonic acid being substituted by alphanaphthylamine disulphonic acids.

The commercial products contain sometimes naphthol-green. They show the following reactions :—Black powder ; aqueous solution, violet ; H Cl, violet solution or violet precipitate ; Na OH, little change or soluble blue precipitate ; solution in H_2SO_4 , pure green to olive-

green; on diluting, it turns at first bluer, and subsequently yields a violet precipitate.

Application.—The naphthol-blacks are used almost exclusively in wool dyeing. Being tetrazo-compounds, they are enabled by their chemical constitution to dye unmordanted cotton; but they possess no importance for this fibre.

The dyeing in copper vessels is liable to give the shade a reddish tone.

Cotton may be dyed with naphthol-black both in an acid bath (with the addition of alum), and in an alkaline bath (with the addition of soap and phosphate of soda).

Wool is dyed by the same methods as with the other acid colours. Naphthol-black is liable to dye unevenly, and the methods indicated for fast red A are advisable for the dyeing with this dyestuff.

Naphthol-black B dyes wool from dark blue to deep black; naphthol-black 6 B gives an excellent black; for a full black shade 5 to 10 per cent. of colouring matter are required. All acid colours can be used for shading; naphthol-green, tartrazin, and azo-flavin (Indian yellow) are especially well adapted for this purpose. The shades produced with naphthol-black on wool are equal to logwood-black in beauty and in fastness to light; they are not sensitive to acids or alkalis, and resist wear and tear, but they are not very fast to milling. Naphthol-black possesses the great advantage over logwood of being dyed in one bath. For these reasons, naphthol-black appears superior to logwood for black dyeing of piece goods, and it has replaced the natural colouring matter to a large extent, the higher price of the artificial product being compensated by its cheaper mode of application.

Silk is not dyed with naphthol-black.

AZO-BLACK (M. L. B.) BLUE-BLACK B (B. A. S. F.)

These two products are very similar in their chemical constitution and resemble naphthol-black. For their production betanaphthylamine is sulphonated, and the mixture of acids thus obtained is diazotised and combined with alphanaphthylamine; the product of this reaction is rediazotised and combined again with betanaphthol disulphonic acid (R salt).

Blue-black powder; aqueous solution, blue-violet; HCl, blue precipitate; NaOH, soluble blue precipitate; solution in H_2SO_4 , bluish-green; on diluting, blue precipitate.

Application and Properties.—Same as naphthol-black.

WOOL-BLACK (Berlin; B. A. S. F.)

Amidoazobenzene disulphonic acid—paratolylbetanaphthylamine.

Blue-black powder; aqueous solution, blue-violet; HCl, red-violet precipitate; NaOH, soluble violet precipitate; solution in H_2SO_4 , blue; on diluting, dark red-violet precipitate. Wool-black is de-

composed on boiling with dilute sulphuric acid, forming amidoazobenzene disulphonic acid and tolunaphthazine (*O. N. Witt*).

Application.—Wool-black is used, as indicated by its name, for wool dyeing. As it is decomposed on boiling with dilute acid, it should always be dyed with the addition of sodium bisulphate, not with sulphuric acid. Enter warm and bring to the boiling point; boil for a long time, turning frequently, since the colour is liable to dye uneven at high temperatures; 4 per cent. of wool-black produces a blue-violet, 8 to 10 per cent. a black shade on wool, which can be toned with other acid dyestuffs. The shade is fairly fast to light, less fast to milling, and not sensitive to dilute acids or alkalies.

NAPHTHYLAMINE-BLACK D (*Cassella*).

Amidoazonaphthalene disulphonic acid—alphanaphthylamine.

The amidoazonaphthalene disulphonic acid, required for the manufacture of this product, is prepared by the action of alphanaphthylamine disulphonic acid on alphanaphthylamine.

Black powder; aqueous solution, dark violet; HCl , dark violet precipitate; NaOH , soluble dark violet precipitate; solution in H_2SO_4 , black-blue; on diluting, at first green solution and afterwards a dark violet precipitate.

Application.—In dyeing with naphthylamine-black D the bath should not become alkaline when in contact with copper or tin. Hence when dyeing in a neutral bath in copper or tin vessels, calcareous water should be neutralised, and $\frac{1}{10}$ per cent. of hydrochloric acid (of the weight of the colour) be added, the dyestuff itself being alkaline; the addition of some ammonium sulphate to the dye-bath is still better.

Cotton can be dyed in a neutral bath with the addition of common salt; but on this fibre no full shades can be produced; only a violet-grey of little practical value is obtained.

Wool is dyed in a neutral bath for light shades and in a bath acidulated with acetic acid for full shades; the bath, however, should not be too acid. The bath is prepared with 10 grms. (1 lb.) of common salt per litre (10 galls.), the required amount of dyestuff, and sometimes 5 to $7\frac{1}{2}$ per cent. of acetic acid (of the weight of the material) are added; for loose wool, the addition of 5 per cent. of alum and 15 per cent. of sodium sulphate to the bath in place of common salt and acetic acid are recommended. The goods are boiled for about $1\frac{1}{2}$ hours.

Naphthylamine-black dyes evenly and yields dark violet to violet-black shades, which are fairly fast to light and to milling, soaping, and rubbing, and not sensitive to dilute acids or alkalies. It is superior to naphthol-black in fastness to milling. For a full shade 4 to 5 per cent. of colour are required; by addition of a green dyestuff a jet-black can be produced.

Silk.—A fine black is obtained on silk with 7 per cent. of naphthylamine-black with the addition of some acetic acid or alum; alum makes

the shade more dead-black than acetic acid. The shade is fairly fast to soap.

JET-BLACK R (Bayer).

This dyestuff is produced by combining diazotised paramidobenzene disulphonic acid with alphanaphthylamine, rediazotising and combining with phenylalphanaphthylamine.

Black powder; aqueous solution, violet-blue; HCl , blue-black precipitate; NaOH , soluble blue-violet precipitate; solution in H_2SO_4 , dark reddish-blue; on diluting, dark blue-green precipitate.

Application.—Unmordanted cotton can be dyed in light shades with 1 per cent. of jet-black, 3 per cent. of borax, and 5 per cent. of common salt; larger quantities of dyestuff do not produce fuller shades. Wool and silk are dyed in a boiling neutral bath, with the addition of 10 per cent. of common salt. The bath is not exhausted and is used continuously; with the addition of acid the bath can be exhausted. Copper vessels should be avoided.

A full blue-black is obtained with 5 to 10 per cent. of dyestuff, which is fairly fast to light and to milling; the shade is not altered by dilute acids or alkalies. A fuller shade can be produced on chromium mordant.

Jet-black G, another brand of the same colouring matter, dyes a dead-black shade.

ANTHRACITE-BLACK B (Cassella).

Amidoazonaphthalene disulphonic acid—

diphenylmetaphenylenediamine.

Brownish-black crystalline powder; aqueous solution, violet-black; HCl , blue; NaOH , dark violet-red precipitate; solution in H_2SO_4 , blackish-blue; on diluting, brownish-olive precipitate; soluble in water with a dark blue colour.

Application.—Anthracite-black is especially valuable for wool dyeing, and is also recommended for silk dyeing.

Wool is dyed with the addition of 10 per cent. of Glaubersalt, and 5 per cent. of bisulphate of sodium in a boiling bath. Goods which are difficult to dye through are first boiled for half an hour with some acetic acid, and then the colour solution is added. Light shades can be produced in a neutral bath with the addition of 10 per cent. of Glaubersalt; calcareous water is neutralised in this case with acetic acid. Anthracite-black produces from light grey to deep blue-black shades on wool; about 5 per cent. are required for a full shade. By the addition of a yellow dyestuff, a dead-black can be produced. The shade is fairly fast to light, milling, and stoving, and not sensitive to dilute acids; alkalies or strong soaping make it a little more bluish.

Anthracite-black can also be dyed on chromium mordants by the same methods as the mordant colours, or, better still, by the method

described for diamine fast red F (p. 419) with chromium fluoride; anthracite-black shades, dyed in an acid bath and saddened with chromium fluoride, are quite fast to milling, and equal to alizarin-black in fastness to light.

Silk is dyed with the addition of tartaric acid; dark blue to black shades are obtained.

VICTORIA-BLACK B (Bayer).

This new colouring matter is produced by combining diazotised sulph-anilic acid with alphanaphthylamine, rediazotising and combining with (1 : 8) dioxynaphthalene sulphonic acid.

Black powder; aqueous solution, dark violet; H Cl , more reddish; Na O H , more bluish; solution in $\text{H}_2\text{S O}_4$, dark green-blue; on diluting, reddish-blue.

Application.—Victoria-black B is dyed on **wool** with the addition of 2 per cent. of sulphuric acid and 10 per cent. of Glaubersalt to the bath; enter at 70° to 80° , bring slowly to the boil, and boil for one hour. A deep bluish-black is obtained which can be shaded with azo-colours, acid green, &c. The colour is very fast to light, acids, and staining, but not quite fast to milling. Victoria-black can also be dyed on aluminium or chromium mordants. On wool mordanted with bichromate or chromium fluoride black shades are obtained which are fairly fast to milling.

Silk is dyed in an acidulated bath of boiled-off liquor or with sulphuric or acetic acid only.

CHROMOTROP 2 R, 2 B, 6 B, 8 B, and 10 B (M. L. B.)

This is a series of new azo-colours, which are produced by combining various diazotised bases with a (new) dioxynaphthalene disulphonic acid (so-called chromotrop acid). They are all uniform substances, and, according to their tinctorial properties, they may be divided into two groups:—Chromotrop 2 R and 2 B belong to one, and chromotrop 6 B, 8 B, and 10 B belong to the other group. They dye both with or without mordants, and may be classed both with the direct and with the polygenetic mordant dyestuffs. The chromotrops are very soluble in water and show the following reactions:—

Chromotrop 2 R.—Dark red powder; aqueous solution, red; H Cl , no change; Na O H , slightly duller; solution in $\text{H}_2\text{S O}_4$, magenta-red on diluting, red.

Chromotrop 2 B.—Snuff-brown powder aqueous solution, red; H Cl , no change; Na O H , dark violet; solution in $\text{H}_2\text{S O}_4$, red-violet; on diluting, red.

Chromotrop 6 B.—Dark brown powder; aqueous solution, bluish-red; H Cl , no change; Na O H , slightly darker; solution in $\text{H}_2\text{S O}_4$, reddish-violet; on diluting, bluish-red.

Chromotrop 8 B.—Dark purple powder; aqueous solution, bluish-

red; H Cl, more bluish; Na O H, slightly darker; solution in $\text{H}_2\text{S O}_4$, blue; on diluting, red-violet.

Chromotrop 10 B.—Dark brown powder; aqueous solution, bluish-red; H Cl, more bluish; Na O H, slightly darker; solution in $\text{H}_2\text{S O}_4$, blue; on diluting, violet.

The dyestuffs are more or less precipitated by stannous chloride and entirely decolorised on being heated with this reagent. They do not yield in aqueous solutions permanent colour lakes; with different metallic mordants, however, differently-coloured compounds are obtained, which can be produced with advantage on dyeing. (See below.)

Application.—The chromotrops are not suitable for the dyeing of cotton or silk; but in spite of their high price they prove very valuable for wool dyeing, especially for mode-colours, owing to their brightness and beauty, fastness to light, dyeing very evenly, and producing various shades according to the methods employed. They are fast to rubbing and stoving, to acids, perspiration, and carbonising, but not very fast to milling, and bleed easily into adjacent white. The chromotrops can be dyed from an acid bath by the same methods as the ordinary acid dyestuffs; the colours which are thus obtained produce with various metallic salts, like those of copper, alum, or chromium, totally different shades. The methods of dyeing the chromotrops on mordants, however, are different from those most generally used for the ordinary mordant colours. While the latter yield the most economical results and best effects by the mordanting and dyeing method (*i.e.*, first mordanting and then dyeing), the chromotrops do not dye evenly on previously mordanted wool and do not exhaust the dye-bath well. The “single-bath” and the “dyeing and saddening” methods only, give satisfactory results with these products. In order to produce certain shades with various mordants they may either be dyed in an ordinary acid bath and subsequently saddened with the metallic salt; or the latter may be added together with the colour solution and the required amount of sulphuric acid to the dye-bath (except for black).

In the following table the methods of dyeing and the changes of colour caused by the most important mordants are indicated.

The red shades, some of which are marked by great brightness, are dyed as shown in the tables in the ordinary way with 4 per cent. of sulphuric acid and 10 per cent. of Glaubersalt, or 15 per cent. of bisulphate of soda.

In dyeing with mordants 4 per cent. of sulphuric acid is used with the amounts of metallic salts given.

Intermediate shades are produced if several mordants are employed together.

Chrome alum gives, as is seen from the tables, the bluest colours, but they are not very level; better results are obtained by using the mixture given of 10 per cent. of alum and 10 per cent. of bichromate of potash.

Chromotrop.	Dyed in acid bath (4% sulphuric acid, and 10% Glauber-salt).	Saddened or dyed direct with 4% sulphuric acid and			Dyed first in acid bath with 3% sulphuric acid, and then, in the same or a following bath, developed with 3% bichromate of potash.
		7½% copper sulphate.	10% alum.	10% chrome-alum or 10% alum + 1 or 1½% bichromate of potash.	
2 R	Scarlet	Dark-red	Claret-red	Prune	Violet-black (dyes very even).
2 B	(like cochineal) Bluish-red	Brown-red	Brown-red	Dark maroon	Deep black (very even, and by gas-light fine black).
6 B	Yellowish magenta-red	Magenta-red	Bluish-magenta	Dark bluish-violet	Greenish-black (little suitable for dyeing, but very good for printing).
8 B	Magenta-red	Dark red-violet	Dark red-violet	Bluish-prune	Black-blue (even dyeing, and by gas-light fine black).
10 B	Bluish magenta-red	Dark red-violet	Dark red-violet	Bluish-prune	Blue-black (even dyeing, and by gas-light fine black).

Stannic chloride does not change the colours, but increases the brightness of both those obtained by means of mordants, as well as those dyed in the ordinary acid baths.

Bichrome is best used as a subsequent saddening; if added to the dye-bath at the beginning the colour suffers in brightness and intensity.

The other acid dyestuffs combine well with the chromotrops. Patent-blue and tartrazin are especially suitable; all shades of dark navy and green-blue, grey, olive, and brown are obtained.

Water containing iron acts strongly on chromotrop 2 R and 2 B dyed in an acid bath, the red becoming dirty and dull. If the water cannot be purified in the usual way, stannic chloride can be used with advantage to counteract the effects of the iron. An addition of 5 per cent. (of the weight of material) is sufficient in most cases to produce good colours. This tin salt is also very well adapted for lightening and brightening colours which, through addition of mordants, have become too dark. In dyeing to shade this fact may be utilised with advantage.

Either wooden or stone vats can be used for dyeing brilliant reds with 2 R or 2 B; the steam pipes must be made of lead or tin.

The reds dyed in an acid bath without mordants are turned somewhat blue by alkalies, 2 B becomes violet. Ammonia is not injurious, since on evaporation of the ammonia the original colour is restored. Lime causes violet or blue spots.

The blacks produced with chromotrops 2 R, 2 B, 8 B, and 10 B, are of special importance; the brand, 6 B, is not suitable for black dyeing, although it yields a good black by printing on wool. As shown in the above table, the blacks are obtained by saddening the previously dyed red with bichromate of potash. In order to obtain good results it is necessary to follow the directions exactly.

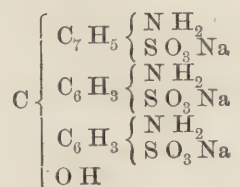
Black Dyeing.—Dye with the addition of 3 per cent. of sulphuric acid, boiling 30 minutes. If the goods are difficult to dye even, work them for half an hour at 75° before adding the acid. After 30 minutes boiling, cool to 75°, add 3 per cent. of bichromate of potash, and boil for $3\frac{1}{4}$ hours; towards the end of the boiling add $\frac{1}{4}$ or $\frac{1}{2}$ per cent. of oxalic acid to check the action of the bichromate so that no severe rinsing will be necessary. A smaller amount of bichromate (or too much oxalic acid) gives a reddish-black, as is also the case if not boiled long enough or with too much water; an excess of bichromate or too long boiling dulls the colour. In dyeing continuously it is preferable to use a separate chrome bath, prepared with 3 per cent. of bichromate of potash and 1 per cent. of sulphuric acid, and to boil for 45 to 60 minutes. It is important that the dye-liquor should reach the actual boiling point, and it is advisable to control the temperature with a thermometer.

In the second bath such acid colours as are not affected by chromic acid, for instance, the Hoechst alizarin-yellows or patent-blues, can be applied for shading.

The chromotrop-blacks are brighter than logwood-black and give a black with a fine blue bloom which does not appear reddish in artificial light; they are superior to chrome-logwood-black in fastness to light; they are fast to acids, carbonising, and stoving, but not quite fast to milling; the black of chromotrop 2 B becomes bluer by alkalies; the others are somewhat reddened, but the original colour is restored by passing through acid.

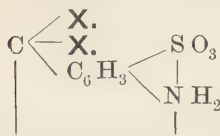
SULPHONATED BASIC COLOURS.

ACID MAGENTA. Acid Rubine; Fuchsine S.



Acid magenta is obtained by the action of fuming sulphuric acid on magenta; it consists of mixtures of the trisulphonic acids of rosaniline and pararosaniline in the form of their sodium or ammonium salts. (See *Magenta*.) The normal salt, as represented by the above formula, is colourless, whereas the acid salts and the acid in the free state are coloured. The colourless salt is constituted analogously to the colourless rosaniline-base, and the coloured compounds have probably a constitution corresponding to the coloured salts of magenta, &c. (See *Magenta*.) The same constitution may be ascribed to the colour

on the fibre. Hence the coloured compounds probably contain the chromophorous group



In which X represents aromatic radicals.

The commercial article is sold in the form of the acid salt, since the normal salt is hygroscopic. The aqueous solution of acid magenta is decolorised on addition of caustic alkalies; the red colour is restored by carbonic acid. Reducing agents transform acid magenta into leucaniline trisulphonic acid, which yields on oxidation the original acid magenta.

Dark green crystalline powder, with a metallic reflex, or dark red powder; aqueous solution, crimson; HCl, no change; NaOH, decolorises the solution almost completely; solution in H_2SO_4 , yellow; on diluting, crimson.

The presence of ordinary magenta in acid magenta can be shown by adding some ammonia and ether to the solution of the dyestuff; ordinary magenta colours the ether yellowish, and the ether when added to acetic acid colours the latter red; pure acid magenta colours neither the ether nor the acetic acid. (*Kertész.*)

Application.—Acid magenta cannot be dyed on cotton or linen. It is used in great quantities for the dyeing of wool and silk, principally for the production of compound shades. As it is dyed by the same methods as the other acid colours, it can be used in the same bath along with them (indigo-carmin included), and has the advantage of dyeing evenly. The shade is similar to ordinary magenta, but it possesses only half the colouring power and not the same brilliancy.

Wool is dyed with the addition of 2 to 4 per cent. of sulphuric acid or sodium bisulphate. If there is a tendency to uneven dyeing 10 to 20 per cent. of Glaubersalt are added; to obtain an even shade acid magenta is also dyed with the addition of 1 per cent. of sulphuric acid and 2 to 5 per cent. of alum. Prepare the bath with the required amount of colour and the other additions, enter the goods at about 40°C ., heat in 40 minutes to the boil, and boil for half an hour. The bath must be distinctly acid; if much colour is left in the dye-liquor, add a little more acid and boil gently till the bath is exhausted.

Acid magenta is not fast to light, but moderately fast to milling, and does not rub. It is, however, decolorised by the action of alkalies (the colour being restored by acids), hence it is not well adapted for goods that have to be milled.

Silk is dyed in a bath of boiled-off liquor that has been slightly acidified with sulphuric acid, or in a slightly acidified bath without boiled-off liquor. Add the colour solution gradually, then heat to the

boil, and continue to boil for 15 to 20 minutes, wash and brighten with sulphuric or tartaric acid, wring, and dry.

Impure Acid Magentas; Grenade S; Maroon S are analogous to the impure ordinary magentas, and are applied in the same way as the acid magenta S.

AZO-CARMIN (B. A. S. F).

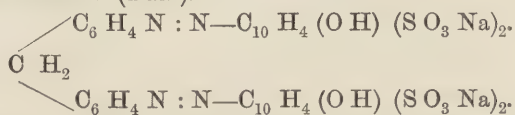
Sodium disulphonate of phenylrosinduline.

Phenylrosinduline, the mother-substance of this dyestuff, is produced by heating *anilidonaphthoquinoneanile* with aniline and aniline hydrochloride to 130° or 160°. Azo-carmin is prepared from this compound with the aid of fuming sulphuric acid.

Red paste with a bronze lustre; sparingly soluble in water; aqueous solution, crimson; H Cl, red precipitate; Na O H, no change; solution in H₂ S O₄, green; on diluting, crimson solution and crimson precipitate.

Application.—Same as acid magenta. The shade is less bluish and less brilliant red than that of this dyestuff. Azo-carmin is fairly fast to light and milling, and is not sensitive to dilute acids and alkalis. It is very valuable in wool dyeing for the production of compound shades, and is an excellent orchil substitute.

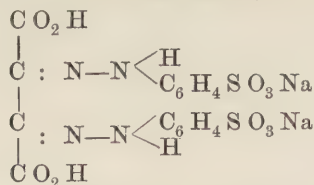
MILLING RED R (Dahl).



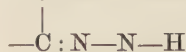
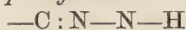
Milling red R is produced by combining one equivalent of diazotised diamidodiphenylmethane with two equivalents of betanaphthol disulphonic acid (R salt).*

Application.—Milling red R is dyed on wool in an acid bath. It produces a scarlet-red shade, which is distinguished by fastness to milling, acids, and bisulphite solution, and is fairly fast to light.

TARTRAZIN (B. A. S. F.; Bindschedler).



Tartrazin is the sodium disulphonate of insoluble tartrazin or *phenylosazonedioxytartaric acid*, an insoluble dyestuff. The group



contains the chromophorous and the auxochromous

* We mention this colour here, since it differs from the ordinary azo-colours by its constitution, and is related to the sulphonated basic colouring matters.

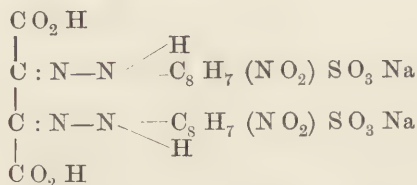
groups. Tartrazin is prepared by heating a solution of dioxy-tartaric acid, with phenylhydrazine parasulphonate of sodium. It is destroyed by reducing agents being resolved into sulphanilic acid and diamidosuccinic acid.

Orange-yellow powder; aqueous solution, yellow; H Cl, the colour is rendered more intense; Na O H, has the same effect as H Cl; solution in $\text{H}_2\text{S O}_4$, orange-yellow; on diluting, yellow.

Application.—Same as naphthol-yellow S and the other acid dye-stuffs.

Tartrazin dyes an orange-yellow shade, similar to flavin, which is exceedingly fast to light and fairly fast to milling. It is used very extensively in wool dyeing.

NITRAZIN-YELLOW (Oehler).



Nitrazin-yellow is obtained by combining dioxytartaric acid with nitroxylylhydrazine sulphonic acid. It is constituted analogously to tartrazin.

Bright orange powder; aqueous solution, yellow; H Cl, no change; Na O H, makes the solution slightly redder; solution in $\text{H}_2\text{S O}_4$, yellow; on diluting, no change.

Application.—Nitrazin-yellow is recommended for wool dyeing by the following methods:—Dissolve the colour in hot water; enter the goods at 50° , and, while heating to the boil, add 3 to 4 per cent. of sodium bisulphate, divided into two portions. 1 to 2 per cent. of acetic acid, instead of bisulphate, will produce a more even shade. The colour is made faster to milling by adding 3 to 5 per cent. of alum or stannic chloride to the exhausted dye-liquor and boiling 15 minutes longer.

Nitrazin-yellow dyes a very bright reddish-yellow, which is very fast to light and fairly fast to milling.

MILLING YELLOW O (Cassella).

The constitution of this dyestuff is not known.

Yellow powder; aqueous solution, yellow; H Cl, reddish-violet precipitate; Na O H, bright yellow precipitate; solution in $\text{H}_2\text{S O}_4$, crimson; on diluting, brownish precipitate.

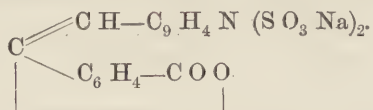
Application.—Milling yellow O is dyed on wool in an acidulated bath with the addition of about 10 per cent. of bisulphate of sodium; it is best to add the bisulphate gradually in several portions and to heat slowly to the boil. Piece goods are first boiled with 10 per cent.

of acetic acid for one hour, after which time the colouring matter is added.

Milling yellow dyes a pure full yellow, which is very fast to light and milling. It can also be dyed on chromium mordants in combination with alizarins and other mordant colours.

Silk is dyed with the addition of acetic acid and with, or without, boiled-off liquor.

QUINOLINE-YELLOW* (B. A. S. F. ; Bayer ; Berlin).

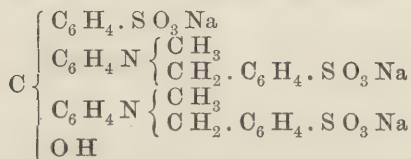


Quinoline-yellow is a mixture of the sodium salts of monosulphonic and disulphonic acids of *quinophthalone*. Quinophthalone (or *quinoline-yellow soluble in spirit*), a yellow basic colouring matter which is not used in dyeing, is produced by heating quinaldine with phthalic anhydride in the presence of zinc chloride to 200°. Quinaldine or methylquinoline ($\text{C}_9\text{H}_6 (\text{CH}_3)\text{N}$) is one of the bases present in small quantities in coal-tar.

Dark yellow powder ; aqueous solution, yellow ; H Cl, light yellow ; Na OH, darker ; solution in H_2SO_4 , reddish-yellow ; on diluting, light yellow.

Application.—Same as naphthol-yellow S. Quinoline-yellow dyes a very bright and fairly fast greenish-yellow on wool and silk. It is an excellent substitute for picric acid in silk dyeing.

LIGHT-GREEN S F (BLUISH) (B. A. S. F.) **ACID GREEN.**



LIGHT-GREEN S F (YELLOWISH) (B. A. S. F.) **ACID GREEN.**
ACID GREEN S O F. LIGHT-GREEN S.

Ethyl-compound, analogous to light-green S F (bluish).

Light-green S F, bluish, and yellowish, are the disulphonic acids of certain compounds of the benzaldehyde-green group. For their production one equivalent of benzaldehyde is heated with two equivalents of benzylmethylaniline or benzyethylaniline respectively, and the products are sulphonated with fuming sulphuric acid. Thus the leuco-compounds are obtained which are converted into the colouring matters by oxidation.

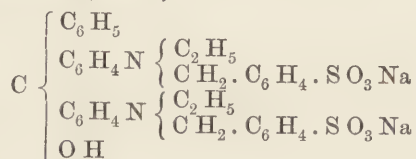
Light-green S F (bluish) forms a brown-black powder, light-green S F (yellowish) a light green powder. Both show the following re-

* The name of this dyestuff is often written erroneously *Chinoline-Yellow*.

actions:—Aqueous solution, green; HCl , brownish-yellow; NaOH , decolorises and produces a dirty-violet turbidity; solution in H_2SO_4 , brownish-yellow; on diluting, green.

Application.—Same as acid magenta; a comparatively large quantity of acid is required in the dye-bath, for wool about double the amount used for acid magenta; in silk dyeing the bath should be distinctly acid. The light-greens dye pure green shades similar to malachite-green; but the dyestuffs possess considerably less colouring power. The shades are moderately fast to light and milling; they are sensitive to the action of dilute alkalies, but not to dilute acids.

GUINEA-GREEN B (Berlin).



This colouring matter is produced by heating benzaldehyde with ethylbenzylaniline sulphonic acid, and oxidising the leuco-compound thus obtained.

Dark green powder; aqueous solution, green; HCl , green; NaOH , black-green precipitate; solution in H_2SO_4 , yellow; on diluting, at first yellowish-red, then yellowish-green, finally green.

Application.—Same as acid magenta.

The shade is similar to that of the light-greens, and behaves similarly towards the various agents.

GUINEA-GREEN B V (Berlin).

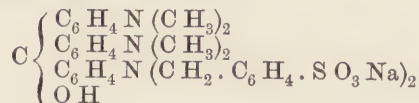
This product is the nitro-compound of the preceding substance, obtained analogously by using metanitrobenzaldehyde instead of benzaldehyde.

Blue-green powder; aqueous solution, green; HCl , blue-green precipitate; NaOH , almost decolorised; solution in H_2SO_4 , brown; on diluting, yellowish-green.

Application.—Same as acid magenta.

Guinea-green B V is very similar to guinea-green B, the shade is more yellowish.

FAST GREEN (BLUISH) (Bayer).



By heating metanitrobenzaldehyde with dimethylaniline, nitro-malachite-green is prepared; this compound is reduced, the amido-group of amido-leuco-malachite-green thus formed is benzylated, and the product sulphonated and oxidised to form the colouring matter.

Dark bluish-green, crystalline powder; aqueous solution, blue-green; H Cl, yellow; on diluting, blue-green; Na O H (on heating only), decolorised; solution in H_2SO_4 , yellowish-red; on diluting, olive to blue-green.

Application.—Same as acid magenta.

Fast green (bluish) dyes a bluish shade of green, which is fairly fast to light and to milling.

ALKALI-BLUE (Nicholson's Blue. Soluble Aniline-Blue).

Alkali-blue is obtained by the action of concentrated sulphuric acid on aniline-blue, soluble in spirit, and consists of the *monosulphonates of mono-, di-, and triphenylrosaniline (and pararosaniline)* in the form of their sodium salts. Triphenylrosaniline (and triphenylpararosaniline) yield the purest blue shades, as is also the case with aniline-blue, soluble in spirit. The brands are indicated according to their shades by letters—*e.g.*, alkali-blue 4 R or 6 B.

Alkali-blue D, which is produced from diphenylamine-blue, is the finest alkali-blue and yields the most greenish-blue shade.

Blue powder; sparingly soluble in cold, freely soluble in hot water; aqueous solution, blue; H Cl, blue precipitate; Na O H, claret-red; solution in H_2SO_4 , red-brown; on diluting, blue precipitate.

Reducing agents convert alkali-blue into the corresponding leuco-compound.

Application.—Alkali-blue is not used in cotton dyeing, as it cannot be permanently fixed on the fibre. It used to be dyed in former years to a limited extent on cotton which had been mordanted with tannin or printed on calico with the aid of tannin and chromium; but it is not so employed now, since many more suitable dyestuffs have been prepared (methylene-blue, Victoria-blue, &c.).

The dyeing with alkali-blue requires a peculiar mode of operation, the colour acid being insoluble in water. The method of dyeing is based on the fact that alkali-blue is taken up by the fibre from an alkaline bath—hence the name—in the form of a colourless salt, and that the coloured compound can be developed on the fibre with the aid of acid. Hence, for dyeing with alkali-blue two baths are required. The constitution of the colourless and the coloured compound is probably analogous to those indicated for the corresponding compounds of acid magenta.

In dyeing with alkali-blue calcareous water should be avoided or purified. The dye-baths are never exhausted and should be used continuously. If a deposit has been formed, the clear liquor may be drawn off for further use; the deposit is dissolved with the aid of a very little soda and added to the clear liquor after filtering.

Wool.—*First Method.*—Prepare the dye-bath with 1 to 3 per cent. of soda ash or 5 to 10 per cent. of borax or silicate of soda or some ammonia, and add the required amount of colour (about 2 per cent.

for a full shade). For the *acid bath* or *developing bath* use about 4 per cent. of sulphuric acid, and the same quantity of alum or sulphate of zinc may be added.

Introduce the wool into the dye-bath at 40°, heat rapidly to the boiling point, and maintain this temperature for about 45 minutes.

In order to match off any given shade, a sample of the material is passed from time to time through the developing bath or through warm dilute acid. When sufficient colouring matter has been taken up the goods are lifted from the dye-bath, wrung out and rinsed in water to remove surface colour; the material has now a dull greyish or pale bluish appearance. Enter the goods into the warm *developing bath*, where they become blue at once; work them for about 15 to 20 minutes, until the shade is fully developed; wash and dry. The developing bath should not be heated above 80°, otherwise the blue is less brilliant; the addition of alum or zinc sulphate to the bath tends to increase the fastness to milling, since these salts form insoluble lakes with the dyestuff. If compound shades are to be produced with the aid of alkali-blue and acid colours, the wool may first be impregnated with the alkali-blue and subsequently passed (without previous developing) into the (acid) bath of the acid colour, where the blue is developed and the second colour is fixed simultaneously. An excess of alkali in the dye-bath (for alkali-blue) is to be avoided, since it has a dulling effect on the shade; some brands of alkali-blue do not require the addition of alkali, or a small amount only.

Second Method.—Work the wool for one hour in a boiling bath which contains 10 per cent. of the weight of the material of borax, wring out, pass into a separate dye-bath (prepared with the required amount of colour), work until a sample acquires the desired shade in dilute acid, wring out and develop as before.

Third Method.—Prepare the dye-bath with 5 per cent. of soap and 2½ per cent. of borax or silicate of soda, dye and develop as by the first method.

Alkali-blue yields fine blue shades, which are superior to the soluble blues in purity and less reddish. The colour is moderately fast to light and fairly fast to milling, and is not affected by dilute acids; by alkalies the shade is decolorised.

Silk and jute are dyed by the third method indicated for wool.

SOLUBLE BLUES.

Methyl-Blue (for Cotton). Soluble Blue. Water-Blue.

Blue for Cotton. Cotton-Blue. China-Blue.

Blue for Silk. Opal-Blue. Guernsey-Blue. Night-Blue.

Light-Blue. Bavarian Blue.

Red-Blue. Serge-Blue. Navy-Blue. Blackley-Blue.

The soluble blues are produced, like the alkali-blues, by heating the aniline-blues, soluble in spirit, with sulphuric acid. A higher temper-

ature (100°), however, is applied, and thus mixtures of di- and trisulphonic acids of triphenyl rosaniline and triphenyl pararosaniline are obtained, the sodium or ammonium salts of which form the commercial soluble blues. As is the case with the alkali-blues, the greenest aniline-blues yield the greenest soluble blues. In addition to this circumstance the purity and the richness of the shade depends upon the degree of sulphonation; the trisulphonates yield less pure and less intense shades than the disulphonates, while both are inferior to the alkali-blues. The disulphonates are less soluble in pure water than the trisulphonates, and it is sometimes advisable to add some soda to the colour solution, and to begin the dyeing without the addition of acid, and to acidulate the bath only after the goods have been worked for some time. The disulphonates can be detected by the fact that they are precipitated from their aqueous solutions by dilute acids.

Of the various blues named above the *Bavarian blues* (produced from diphenylamine-blue), *blue for silk*, and *opal-blue* are chiefly used for silk dyeing, and give more or less greenish-blue shades; the other blues are principally dyed on wool, but they are also applied to silk and cotton. The trisulphonates are better adapted for wool dyeing and the disulphonates for silk dyeing; no strict distinction, however, is made.

The last-named blues, *red-blue*, &c., are the reddest products.

The shades are also distinguished by letters, from 4 R to 6 B, and the qualities by the numbers OO, O, I, II, III, IV; number OO being the purest and greenest product, the others being gradually duller and redder. The prices of the soluble blues vary widely, and the value of the different commercial products can only be determined by comparative dye-trials.

The soluble blues show the following general reactions:—Blue powders or irregular lumps; aqueous solution, blue; H Cl, not much change, or blue precipitate (see above); Na O H, claret-red to red-brown; solution in $H_2S O_4$, brownish-yellow to brown-red; on diluting, blue solution or blue precipitate.

On reduction, the soluble blues form leuco-compounds which are reconverted into the original dyestuffs by oxidising agents. The constitution of the coloured compounds is probably analogous to that of acid magenta.

Application.—The soluble blues are dyed both on the vegetable and animal fibres.

Cotton is dyed by various methods, but the shades produced are not fast. Since the introduction of methylene-blue and Victoria-blue this fibre has been dyed to a very limited extent only with soluble blues.

First Method.—Mordant with tannin and antimony as indicated for the basic colours (p. 452), and dye in a lukewarm bath with the addition of 2 to 3 per cent. of alum, heat to 60° to 70°, wring and dry, without washing. The shade is not fast.

Second Method.—Mordant first in a warm soap-bath containing $2\frac{1}{2}$ grms. (4 oz.) of soap per litre (10 galls.), working the cotton in the warm bath for 15 minutes, wring, and pass without washing into a bath of stannic chloride (4° Tw.), work for half an hour, and wash thoroughly in water. Dye in a lukewarm bath, with the addition of 2 to 3 per cent. of alum. The shade is greener than that obtained by the preceding method, and fairly fast to light; it does not resist washing or soaping.

Third Method.—Mordant with tannin, and fix with basic alum (2° Tw.), (p. 454), wring without washing and dye, heat slowly to 60° or 70° . Or the cotton is mordanted with tannin alone, and dyed with the addition of 2 to 4 per cent. of alum. No fast shades are obtained.

Fourth Method.—Soap the cotton as by the second method, and dye with the addition of acetic acid or alum. Light tints only are obtained, which are very fugitive.

As the dye-bath is never exhausted, it should be preserved for further use.

Wool is dyed with the addition of 2 to 4 per cent. of sulphuric acid, and 5 per cent. of Glaubersalt. By the addition of a small quantity of stannic chloride and alum, more even and brighter shades are produced. Add the colour solution to the tepid bath, introduce the goods, heat slowly to the boil, boil for half an hour, let cool to 80° , wash and dry.

Soluble blue on wool is slightly inferior to alkali-blue in fastness to light and milling. Soluble blues are used largely for the production of navy blues on heavy woollen goods.

Silk is dyed with the soluble blues in a boiled-off liquor bath, which has been slightly acidulated with sulphuric acid. Add the colour solution to the bath, heat slowly to the boiling point, and maintain this temperature until the desired shade is obtained; wash, brighten in sulphuric acid, and dry.

Jute is dyed with the addition of $\frac{3}{4}$ to $1\frac{1}{2}$ per cent. of alum, and $\frac{1}{8}$ to $\frac{1}{4}$ per cent. of sulphuric acid; boil for 20 to 25 minutes, let cool to 40° to 60° , wring and dry without washing.

HOECHST NEW BLUE (M. L. B.)

This dyestuff is totally different from the basic new blues, and belongs to the class of "soluble blues" just described. For its production trimethyltriphenylpararosaniline is prepared by the action of phosgene gas (COCl_2) on methyldiphenylamine; and the compound thus obtained is converted with sulphuric acid into sulphonic acids. The commercial article is the lime salt of the disulphonic and trisulphonic acid.

Dark blue powder; aqueous solution, blue; HCl , blue solution and some precipitate; NaOH , decolorised; solution in H_2SO_4 , brown-red; on diluting, blue solution and precipitate.

Application.—Hoechst new blue is chiefly used in wool dyeing.

It can be dyed by the same methods as the soluble blues. The following mode of procedure, however, is advisable, since the dyestuff is very apt to dye unevenly.

Dye for 2 to 3 hours in a boiling neutral bath with about one-third more of colouring matter than the shade requires, rinse, and develop in a fresh acid bath. The dye-bath is not exhausted and is used continuously. This method is the best for goods which are apt to dye unevenly.

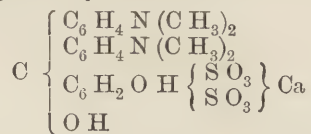
Loose wool and other goods are dyed with advantage by the fourth method given in the beginning of this chapter (p. 507); the dye-bath is fairly well exhausted. The fifth and sixth methods also give very good results, but the baths are not so well exhausted.

Hoechst new blue dyes pure blue shades on wool, which are moderately fast to light and fairly fast to milling.

Silk is dyed in a boiled-off liquor bath which has been slightly acidulated with sulphuric acid. Add the colour gradually to the luke-warm dye-bath and heat gradually to the boiling temperature; boil a short time, wash, brighten with sulphuric acid, wring, and dry.

PATENT-BLUE (M. L. B.)

Patent-blue comes into the market in several brands (superfine, extra, B. N., &c.), which are calcium salts of sulphonic acids of metaoxy-, metaamido-, or metachlor-tetraalkyldiamidotriphenylcarbinol. Their constitution is exemplified by the formula:—



For their production one equivalent of metanitrobenzaldehyde is condensed with two equivalents of dimethyl- or diethyl-aniline; the product is reduced so as to convert the nitro-group into the amido-group; by subsequent sulphonation and oxidation of the leuco-compounds the colouring matters are obtained.

Blue or coppery-red powder; aqueous solution, blue; HCl, olive-green to yellow; NaOH, makes more bluish, on heating violet; solution in H₂SO₄, pale yellow; on diluting, deep yellow to greenish-blue.

Application.—The patent-blues are used for the dyeing of wool and silk, and are applied by the usual methods employed for the acid dyestuffs. They dye very evenly and well through; the materials may be introduced into the boiling bath. The shade is somewhat sensitive to the action of copper salts. The baths are not well exhausted and should be kept concentrated. For silk dyeing not too much sulphuric acid should be used for the acidifying of the boiled-off liquor; else the shade will be less pure.

The colours can also be dyed on chromium mordants.

The patent-blues produce pure blue to greenish-blue shades which do not lose in purity and brightness, and do not appear redder but

greener in artificial light. They are slightly faster to light than indigo-carmin, but not to milling; the shades are not very sensitive to dilute alkalies.

CYANIN B (M. L. B.)

This new colouring matter is produced by oxidising one of the patent-blues by means of ferric salts or chromic acid; its exact constitution is not yet known. It is very similar to the patent-blues.

Application.—Same as other acid colours. Calcareous water should be acidulated with acetic acid before the sulphuric acid or bisulphate is added; otherwise the colours will be dull and dirty. Cyanin B dyes evenly, and produces a bright greenish-blue, similar to the patent-blues in appearance and properties; the tone, however, does not appear to vary so much in artificial light.

GALLANILIC INDIGO P S (Durand).

This colour is related to gallocyanin, gallanilid-violet, and gallanilid-blue. For its production gallanilide is heated with nitrosodimethylaniline; the product is subsequently phenylated by treatment with aniline, and finally converted into a sulphonic acid.

Dark blue paste; aqueous solution, indigo-blue; H Cl, dark brown precipitate; Na O H, soluble blue precipitate; solution in H_2SO_4 , brown; on diluting, brown precipitate.

Application.—Gallanilic indigo P S is dyed on wool with the addition of sulphuric acid and Glaubersalt, and yields very fine shades resembling those of indigo-carmin, but faster to light. It will doubtless prove a very valuable substitute for this colour, if it can be offered at a lower price than at present.

THIOCARMIN R (PASTE) (Cassella).

Thiocarmin R is chemically related to methylene-blue, being a sulphonated *thionine*. It is prepared analogously to methylene-blue by using ethylbenzylaniline sulphonic acid. The exact composition of the dyestuff, which has been recently introduced into commerce, is not known yet.

Dark green paste; aqueous solution, bluish-green; H Cl, no change; Na O H, makes the solution slightly greener; solution in H_2SO_4 , bright green; on diluting, deep blue.

Application.—Same as acid magenta or other acid colours. Thiocarmin dyes greenish-blue shades on wool, and is recommended as a substitute for indigo-carmin. It dyes evenly, and is suitable for the production of compound shades, modes especially in combination with acid azo-colours. The shade is inferior to patent-blue or indigo-carmin in resistance to light, and moderately fast to milling.

INDULINE (soluble in water). **FAST BLUE.** **INDIGO-SUBSTITUTE.** **NIGROSINE.**

The *indulines* and *nigrosines*, soluble in spirit (p. 490), are converted

by the action of sulphuric acid into sulphonic acids, which are soluble in water, and can be dyed by the same methods as the acid colours.

The commercial brands, which give various shades of dark indigo-blue, are known as fast blue R to 3 R or induline N N for the reddish shades, and fast blue B or greenish, and induline 3 B and 6 B for the blue shades. Nigrosine, which also belongs to these dyestuffs, dyes greyish-blue shades.

Brown to black powder, with a bronze lustre; aqueous solution, violet-blue; HCl , more bluish, or a blue precipitate is formed; NaOH , soluble brown-violet precipitate; solution in H_2SO_4 , blue; on diluting, violet-blue, or blue precipitate.

Induline forms on reduction a leuco-compound, which is reoxidised by the action of the air.

The degree of sulphonation of the commercial products varies; some resemble alkali-blue and can be dyed in a similar manner; most brands are more similar in this respect to the soluble aniline-blues.

The indulines show a singular behaviour towards the wool fibre* which is apparently founded on their chemical constitution. They produce no patches like other "uneven" colouring matters; it is the single wool fibre which is dyed unevenly by the indulines, as can be seen under the microscope; the roots of the wool fibres take up the colour pretty easily, whilst the more horny portions take it up very slowly or not at all. The speckled effect thus produced, which is called "*piqué*" by the French dyers, has prevented the general employment of these valuable dyestuffs. In this case the remedy will have to be applied to the fibre, not to the colouring matter or the dyeing process. Coarse wools dye better with the indulines than the fine qualities. If the wool be boiled in dilute solutions of soda, borax, or sodium stannate, it will afterwards dye more easily with induline. Under the influence of the alkali the scales of the wool fibre open out and the colour solution is consequently able to penetrate more easily into the interior of the fibre. This method, however, has not found much favour with dyers, who naturally fear the injurious effect of hot alkaline liquids on wool. Of much more importance is the effect of another method, used especially in wool-printing, which consists in chlorinating the wool by steeping it alternately in a dilute solution of bleaching powder and dilute hydrochloric acid. Wool treated in this manner undergoes a great change and is rendered somewhat similar to silk; it loses, however, greatly in milling capacity. (See below.)

Application.—Induline is used to a small extent in cotton dyeing, more for wool, but principally for silk dyeing.

Cotton is mordanted with tannin and antimony and dyed at the boil with the addition of a little sodium bisulphate. A dark indigo-blue shade is obtained which does not resist washing well, but is very fast to light.

* O. N. Witt, *Journ. Soc. Dyers and Col.*, 1890, p. 42.

The colour can also be fixed to some extent on unmordanted cotton.

Wool.—To obtain even colours on wool slow and very hot dyeing is of great advantage. If the induline is only slightly soluble in acidulated water the method indicated for alkali-blue may be employed. The readily soluble indulines are dyed in a rather concentrated neutral bath, and after the goods have been boiled for some time, 5 per cent. of sodium bisulphate is gradually added. It is, however, advisable to use in this case also a separate bath with sodium bisulphate, since the dye-bath is not well exhausted. The methods indicated for Hoechst new blue (p. 548) are also applicable.

Fine dark indigo shades of considerable fastness are obtained by the following method :—Dye in a bath containing 2 to 5 per cent. of induline and 5 per cent. of ammonium oxalate (or 3 per cent. of oxalic acid), heat to the boiling point, and boil for 2 to 3 hours, wash, and enter into a hot bath containing 5 per cent. of sodium bisulphate. The colour is almost entirely developed in the first bath ; in the second bath the blue can be shaded with other acid dyestuffs. The employment of ammonium oxalate produces darker shades of indigo-blue.

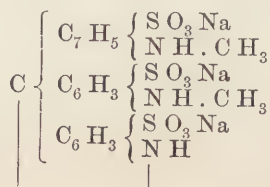
The chlorinating of the wool which has been mentioned above is done by steeping the wool for a short time in a clear solution of chloride of lime ($\frac{1}{2}^{\circ}$ Tw.), passing through hydrochloric acid ($1\frac{1}{2}^{\circ}$ Tw.), and thoroughly washing in water. A better mode of procedure is to dissolve a very small amount of chloride of lime in hydrochloric acid (3° Tw.), to work the wool in this bath for a very short time and then wash thoroughly in water. Very even shades are obtained by this mode of preparation. The process, however, is not suitable for goods which have to be milled, since the wool loses its milling capacity and the colour is also less fast to milling.

Induline yields dark indigo-blue shades which are very fast to light and fairly fast to milling ; they are not sensitive to acids and alkalies.

Silk does not offer the same difficulties to dyeing with induline as wool. It is dyed in a boiled-off liquor bath which has been made distinctly acid with sulphuric acid. Add the colour solution, raise the temperature to the boiling point, work for half an hour, wash, and brighten with sulphuric acid, wring, and dry.

Induline has replaced indigo-carmin to a very great extent in the production of mixed shades on silk, since it is very fast to light.

RED-VIOLET 4 R S (B. A. S. F.)



Red-violet 4 R S is prepared by the action of fuming sulphuric acid on dimethylrosaniline, and is the sodium trisulphonate of this base.

Red-violet powder; aqueous solution, crimson; H Cl, no change; Na O H (on heating), light reddish-yellow; solution in $\text{H}_2\text{S O}_4$, brown-yellow; on diluting, crimson.

Application and Properties.—Same as acid magenta. Red-violet 4 R S dyes a bluish shade of red, a little more bluish than acid magenta. The shade is moderately fast to light and milling, but very sensitive to soda, ammonia, or alkaline road dirt.

Red-violet 4 R S and 5 R S can also be dyed on chromium mordant; this variety is common to the various acid violets.

RED-VIOLET 5 R S (B. A. S. F.)

Red-violet 5 R S is the sodium trisulphonate of monoethylrosaniline, prepared analogously to red-violet 4 R S.

Brown-violet lumps with a metallic reflex; aqueous solution, crimson; H Cl, no change; Na O H, light brown-yellow; solution in $\text{H}_2\text{S O}_4$, yellow; on diluting, crimson.

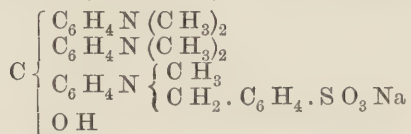
Application and Properties.—Same as red-violet 4 S R; the shade is slightly more bluish.

ACID VIOLET 2 B (B. A. S. F.)

This product is the sodium salt of the sulphonic acid of ordinary methyl-violet, and is produced by the action of sulphuric acid on this colouring matter.

Application and Properties.—Acid violet 2 B is similar to red-violet 4 R S, but dyes a bluer shade of violet than this colouring matter.

ACID VIOLET 4 B N (B. A. S. F.) ACID VIOLET 6 B (Bayer).



This product is obtained by the sulphonation of benzylpentamethyl-pararosaniline (prepared by the condensation of tetramethyldiamidobenzophenone chloride and benzylmethylaniline), or by the sulphonation and subsequent oxidation of the leuco-compound of the above-named base.

Blue-violet powder or crystals; aqueous solution, blue-violet; H Cl, blue precipitate, which dissolves on diluting with an olive colour, the solution becoming first green and then blue; Na O H, blue precipitate; on heating, colourless solution; solution in $\text{H}_2\text{S O}_4$, brownish-orange; on diluting, at first olive, then green, at last blue.

Application.—Same as acid magenta. Acid violet 4 B N dyes a bluish-violet shade; it dyes evenly, is fairly fast to milling, and not so sensitive to soda, ammonia, or road dirt as red-violet 4 R S.

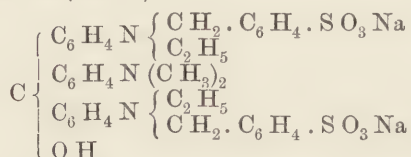
Acid violet 4 B N is moderately fast to light, being superior in this respect to the basic violets.

The acid violets are principally used as substitutes for indigo-carmin for the production of compound shades, and are dyed in combination with other acid colours, such as light green, acid magenta, naphthol-yellow, and the oranges. The acid violets can be dyed on chromium mordant, as has been stated above.

WOOL-BLUE S (B. A. S. F.)

Wool-blue S is a mixture of acid violet 4 B N and light green; it serves as a substitute for indigo-carmin.

ACID VIOLET 6 B (Berlin).



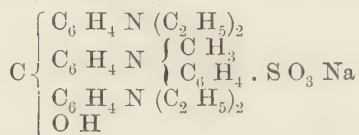
Acid violet 6 B is prepared by the oxidation of the leuco-compound which is obtained by condensation of dimethylpara-amidobenzaldehyde and ethylbenzylaniline sulphonic acid.

Blue-violet powder; aqueous solution, violet; H Cl, bluish-green; Na O H, decolorises; diluted solutions are light blue; solution in H₂ S O₄, yellowish-brown; on diluting, from dark brown to bluish-green.

Application.—Same as acid magenta.

Acid violet 6 B is similar to acid violet 4 B N.

ALKALI-VIOLET (B. A. S. F.)



Alkali-violet is prepared by the sulphonation of methylphenyltetraethylpararosaniline (prepared by condensation of tetraethyldiamidobenzophenone and methyldiphenylamine).

Violet powder; aqueous solution, violet; H Cl, olive-green; on diluting, blue; Na O H, soluble blue precipitate; on heating, the solution is decolorised; solution in H₂ S O₄, yellow-brown; on diluting, at first olive, then blue.

Application.—Alkali-violet can be dyed in an alkaline, neutral, or acid bath, and is applicable to cotton, wool, or silk. It can, therefore, be used for the purpose of reddening alkali-blue, or in conjunction with colours which dye in a neutral bath, or, finally, in an acid bath along with the different colours. It can be used in combination with fast green and light green for the production of indigo-blue and navy-

blue shades, or in conjunction with red and yellow dyestuffs, in order to obtain browns, olives, &c. When dyed alone it produces a pure blue-violet shade.

Cotton is dyed with alkali-violet by the usual method employed for the basic colours on a tannin and antimony mordant; the shade is moderately fast to soaping, and a little faster to light than methyl-violet. (See pp. 451 and 497.)

Wool is dyed best in a boiling bath by the same methods as alkali blue or in a neutral bath like the methyl-violets.

In an acid bath alkali-violet is dyed on wool according to the requirements of the acid colours with which it is combined; in this case it should not be dyed very rapidly. Alkali-violet on wool is very fast to milling.

Silk is dyed with alkali-violet in a boiled-off liquor bath, slightly acidulated with sulphuric acid. Add the colour solution, enter the silk, heat to the boiling point and work at this temperature for half an hour, wash, brighten in sulphuric acid, wash, and dry. The shade is fast to water and soap.

Silk can also be dyed with alkali-violet in a neutral bath or by the method used for alkali-blue.

REGINA-VIOLET, SOLUBLE IN WATER (Berlin).

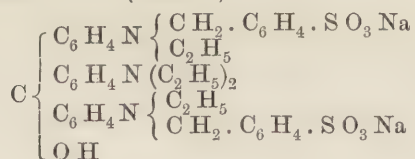
Regina-violet is obtained by the sulphonation of a bye-product obtained in the manufacture of magenta by the nitrobenzene process. It is probably the sodium trisulphonate of diphenylrosaniline.

Lumps or powder with a bronze reflex; aqueous solution, violet; H Cl, precipitation of the sulphonic acid; Na OH, makes the colour lighter, but does not decolorise.

Application.—Same as acid magenta.

Regina-violet dyes a red-violet shade.

FORMYL-VIOLET S 4 B (Cassella).



Formyl-violet S 4 B is a rosaniline-violet, produced by oxidising together diethyldibenzylidiamidodiphenylmethane disulphonic acid and diethylaniline.

Red-violet powder with a bronze reflex; aqueous solution, violet; H Cl, yellow, almost decolorised; Na OH, solution in H₂SO₄, orange-yellow; on diluting, yellow to colourless.

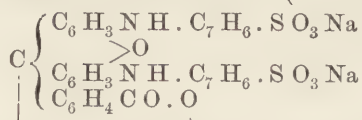
Application.—Same as acid magenta. Formyl-violet S 4 B dyes a full bluish shade of violet, which resembles the better kinds of acid violets as regards fastness to light, milling, acids, and alkalies (road

dirt). It dyes evenly, and is useful for compound shades, as a substitute for indigo-carmin, &c.

Formyl-violet can also be dyed on chromium mordants.

The colour is fairly fast to washing on silk.

VIOLAMIN R or **FAST ACID VIOLET R** (M. L. B.)



Violamin R is produced by the action of orthotoluidine on fluorescein chloride, and subsequent sulphonation of the compound. It is *diorthotolylrhodamine disulphonate of sodium*, and has probably the constitution shown by the above formula.

Light maroon powder; aqueous solution, red, with an orange fluorescence which disappears on heating and reappears on cooling; HCl, pink precipitate; NaOH, no change; solution in H₂SO₄, orange; on diluting, red precipitate.

Application.—Same as acid magenta. Violamin R produces a bluish-red, which is similar to, but bluer than, rhodamine. It dyes evenly, and is fairly fast to light and milling, and the shade is not affected by dilute alkalies. The dyestuff is, in spite of its high price, extremely valuable for the dyeing of wool and silk, especially for the production of mode colours.

VIOLAMIN B or **FAST ACID VIOLET B** (M. L. B.)

Violamin B is *diparatolylrhodamine disulphonate of sodium*, and is produced analogously to violamin R by substituting paratoluidine for orthotoluidine.

Maroon powder; aqueous solution, reddish-violet; HCl, purple precipitate; NaOH, cherry-red; solution in H₂SO₄, red-orange; on diluting, red violet precipitate.

Application and Properties.—Same as violamin R. The shade is violet. It may be dyed on silk which has been weighted with tin.

WOOL-GREY R, B, and G (M. L. B.)

These three dyestuffs are produced by the action of aniline or paratoluidine, on the products which are obtained by condensation of nitrosodimethylaniline or nitrosodiethylaniline with betanaphthol sulphonic acid S.

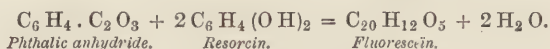
Application.—The wool-greys are dyed from acid baths, and are suitable for mode colours in wool dyeing. They produce reddish-, bluish-, and yellowish-grey shades, which are not fast to light.

THE EOSINS AND RHODAMINES.

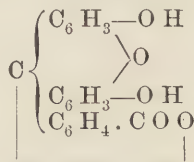
The dyestuffs which are described in this chapter are closely related to each other by their chemical constitution; they dye shades ranging

from yellow to bluish-red, which are distinguished by an extraordinary brilliancy.

All the eosins are derivatives of fluorescein, which is produced by the condensation of phthalic anhydride, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O$ and resorcin:—



Fluorescein is a derivative of triphenylmethane carboxylic acid.



The various commercial eosins are the alkali salts of chlorine-, bromine-, iodine-, or nitro-substitution derivatives of fluorescein or the methyl- and ethyl-ethers of fluorescein and some of these derivatives; chrysolin is a benzylated fluorescein, and cyclamin is a sulphur derivative.

Rhodamine B is obtained like fluorescein by the condensation of phthalic anhydride with a phenol, diethylmetamidophenol being made to react instead of resorcin. Rhodamine S resembles this dyestuff both constitutionally and in its chemical properties; it is not produced, however, from phthalic anhydride, and does not belong to the triphenylmethane group. It is formed by the condensation of succinic anhydride

$C_2H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} O$ with diethylamidophenol and is a derivative of diphenylmethane (the constitutional formula for which is given on p. 565, rhodamine S). The composition of rhodamine G has not been made known; it seems to be closely related to the other rhodamines. The commercial rhodamines are the basic (*i.e.*, monacid) hydrochlorides of (diacid) organic bases.

All the compounds of this group are converted into leuco-compounds by reduction, and regenerated more or less rapidly by oxidation; but the original dyestuffs are not always reproduced, since the substituting groups—such as bromine or iodine—are frequently eliminated by the reducing agents.

The colours are mostly soluble in water and in dilute alcohol; those which are sparingly soluble in water are dissolved in alcohol before use: *spirit-eosins*. The solutions show more or less intense fluorescence, which is strongest in alcoholic solutions (the erythrosins do not fluoresce in aqueous solutions, and eosin B N very little).

The colours of this group dissolve in concentrated sulphuric acid with a yellow colour, while they vary in their reactions towards hydrochloric acid and caustic soda according to their phenolic or basic character. Fluorescein and its derivatives remain in solution on addi-

tion of caustic soda and are precipitated by hydrochloric acid; the reverse reactions take place with the rhodamines. Chloride of lime decolorises the solutions on heating. The eosins form lakes with various metallic salts, especially with lead salts; some of these are extensively used on account of their great brilliancy as pigments (vermilionettes). Most of the eosins may be recognised by the fluorescence of their solutions, especially in the presence of ammonia; those which do not fluoresce yield, when reduced and reoxidised, the intensely fluorescent fluoresceïn and they can be detected in this way. The rhodamines evince fluorescence in aqueous solutions. The eosins and rhodamines are readily distinguished by their phenolic or basic characters respectively. If the bromine or iodine derivatives of fluoresceïn are dissolved in strong sulphuric acid and the solution is heated, bromine or iodine escapes; the former can be detected by the smell, the latter by the reaction on moistened starch paper and by the evolution of violet vapours.

The eosins which are freely soluble in water are stripped from the fibres by dilute alkalies, the spirit-eosins by alcohol; the rhodamines are extracted to some extent both by alkalies and by alcohol. The dyestuffs can be recognised by their fluorescence, &c., in the solutions thus obtained.

The quality and strength of the eosins and rhodamines are estimated by dye-tests. The eosins can be dyed on unmordanted cotton with the addition of common salt—as described below; the rhodamines are better tested on wool or silk.

Application of the Eosins and Rhodamines.—The eosins and rhodamines can be dyed both on the vegetable and on the animal fibres. The eosins have been valued very highly for the brilliancy of their shades, which is surpassed by no other group of colours. They are still used for this reason in silk dyeing, especially the spirit-eosins, which give brighter colours than the soluble eosins, and are distinguished by a very intense fluorescence. In the dyeing of wool and cotton, however, they have been replaced to a great extent by other dyestuffs, which are both less fugitive and less expensive; frequently the property of fluorescing is objectionable. Indeed, the eosins are rarely dyed on wool, and to a limited extent only on cotton, since the azo-dyestuffs have come into the market. The before-mentioned lakes (vermilionettes) are still largely employed as steam colours in calico-printing (especially to produce reds on indigo-blue). These lakes are used, however, in much larger quantities for the colouring of paper and for painting; they are of great value for these purposes, not only on account of their extraordinary brightness, which rivals that of genuine vermilion, but also for their great fastness to light (in contrast with the eosins which are dyed on the textile fibres).

The rhodamines are not inferior to the eosins in beauty and brilliancy of shade, and they evince also strong fluorescence on the

fibres. Rhodamine B and G are not of great value for the dyeing of cotton, since they cannot be fixed on this fibre permanently without losing their brilliancy; they possess, however, considerable fastness both to light and to soap on silk and wool, and they are used with advantage to produce brilliant red shades on these fibres. Rhodamine S is recommended for the dyeing of cotton and silk mixed goods.

The eosins soluble in water require 30 parts of hot water for solution. Since they form insoluble lakes in hard water, soft water or water which has been boiled off with sodium carbonate should be used; the latter may be employed in its weakly alkaline state. The eosins, soluble in spirit, are dissolved in diluted methylated spirits, as described on p. 451. The rhodamines are dissolved, like the basic colours, with about 250 parts of hot water.

Application on Cotton and Linen.—*First Method.*—The dye-bath is prepared with a lukewarm solution of common salt to stand at 7° Tw.; the colour solution is added and the material turned in the liquor at 40° to 50° for 45 minutes, then wrung, and dried without washing. The bath should be very concentrated and be kept for further use. Light shades only can be produced, and the colour is stripped by rinsing with water.

Second Method.—The material is first worked in a lukewarm bath of sodium stannate and, after steeping for 2 to 3 hours, treated for about the same time in a bath of basic alum. After this it is wrung, dyed as by the first method, and dried without washing. All the liquors should be very concentrated; the dye-bath is not exhausted. The shade is not fast to soap, but faster to rinsing with water and more intense than that obtained by the first method. Use for 10 kgs. (10 lbs.) cotton

$\frac{1}{2}$ kg. ($\frac{1}{2}$ lb.) of stannate of soda,
 $\frac{1}{2}$ kg. ($\frac{1}{2}$ lb.) of alum, and
 100 grms. (1½ oz.) of soda crystals;

dissolve the alum and the soda crystals separately, and mix the solutions.

Third Method.—The goods are saturated with a solution of Turkey-red oil—50 grms. per litre ($\frac{1}{2}$ lb. per gall.)—wrung, dried or steamed, turned for half an hour in acetate of alumina (3° Tw.), dried, passed through a weak chalk bath, and well washed in water. After this the material is dyed as by the first method. A hot strong solution of soap may be used with similar results instead of the Turkey-red oil. The dye-bath is not exhausted, and the shades resemble, both in appearance and in fastness, those obtained by the second method.

More bluish shades are produced with the eosins if a solution of a basic lead salt (at about 3° Tw.) is substituted for the red liquor. The goods may also be impregnated first with the lead salt, passed through ammonia, washed in water, and then dyed.

The use of lead salts has the disadvantage that the colour is blackened by sulphuretted hydrogen.

Application to Jute.—Jute is dyed at the boil with the addition of some alum and acetic acid, washed and dried.

Application to Wool.—Wool is dyed at the boil with the addition of acetic acid or alum. Alum gives the brighter shades, but the wool has a harsher feel than when dyed with the addition of acetic acid. Boil for 20 minutes, wash and dry. Better results are obtained by the following method:—Prepare the bath for 10 kgs. (10 lbs.) wool with

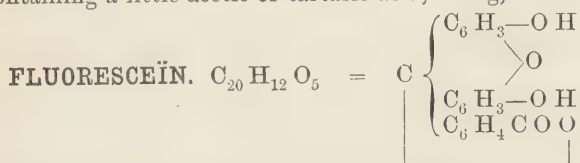
200 litres (20 galls.) of water,
 $\frac{1}{2}$ kg. ($\frac{1}{2}$ lb.) of acetic acid,
 300 grms. (5 oz.) of tartar, and
 $\frac{1}{2}$ kg. ($\frac{1}{2}$ lb.) of acetic acid;

work the wool for half an hour in this bath at the boil, allow to cool, add the colour solution, turn quickly for 15 minutes, heat gradually to boiling, turn for 15 minutes more, wash, and dry. The bath is exhausted, if it is sufficiently acid; otherwise more acetic acid may be added. The eosins are very fugitive to light; the rhodamines are greatly superior in this respect.

Application to Silk.—Silk is dyed in a bath of boiled-off liquor which has been acidulated with tartaric or acetic acid. Use for 10 kgs. (10 lbs.) of silk

30 litres (3 galls.) of boiled-off liquor,
 270 litres (27 galls.) of water,

and sufficient acid to make the bath slightly acid; add the colour solution, turn the silk while heating to the boil, and work for half an hour in the boiling bath; wash, and brighten in a warm bath containing a little acetic or tartaric acid, wring, and dry.

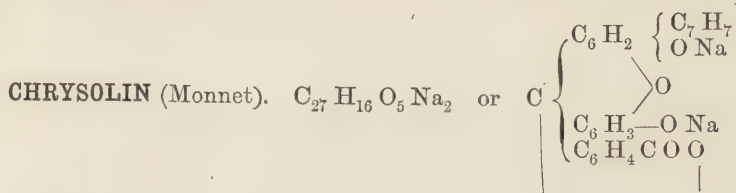


Fluorescein, the mother-substance of the eosins, is produced by heating 1 molecule of phthalic anhydride and 2 molecules of resorcin to 200° C. in the presence of zinc chloride. It forms a dark yellow crystalline powder, which is very sparingly soluble in the usual solvents, except hot glacial acetic acid. It possesses little tinctorial power and is not a commercial article.

URANIN ($\text{C}_{20}\text{H}_{10}\text{O}_5\text{Na}_2$).

Uranin is the sodium salt of fluorescein. Yellowish-brown powder; aqueous solution, yellow with intense green fluorescence; HCl, yellow flocculent precipitate; NaOH, darker with a dark green fluorescence; solution in H_2SO_4 , yellow; on diluting with water, yellow.

Uranin dyes wool and silk yellow, and is used to a very limited extent in wool printing.



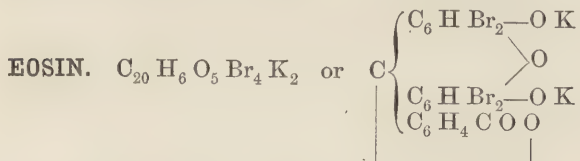
Chrysolin, the sodium salt of a benzylated fluoresceïn, is produced by heating phthalic anhydride, resorcin, and benzyl chloride together in the presence of sulphuric acid.

Reddish-brown powder or lumps with a greenish reflex; aqueous solution, brown with a green fluorescence; HCl , brown-yellow precipitate; $NaOH$, darker; solution in H_2SO_4 , yellow; on diluting, yellow precipitate.

Chrysolin dyes a yellow shade which is very similar to turmeric; the colour is moderately fast to light on the animal fibres. It is used sometimes in cotton dyeing for topping quercitron-yellow.

Aureosin, a chlorinated fluoresceïn, and **Rubeosin**, a nitrated aureosin, have disappeared from the market.

Eosin-Orange and **Eosin 3 G** are mixtures of dibrom- and tetrabromfluoresceïn, and are not regular commercial articles.



Eosin, yellowish; **Eosin**, soluble; **Eosin G**, **Eosin J**, **Eosin A**, **Eosin B**, &c.

Eosin is the potassium- (or sodium-) salt of tetrabromfluoresceïn, and is produced by the action of bromine on fluoresceïn.

Eosin comes into the market in the form of small red crystals with a bluish reflex, or as a dark red amorphous powder, and is completely soluble in three times its weight of water, with a red colour; the dilute aqueous solution is pink-coloured with an intense yellowish-green fluorescence. The alcoholic solution evinces a still more intense fluorescence. Mineral acids precipitate from the aqueous solution of eosin tetrabromfluoresceïn in the free state as an amorphous orange-coloured powder, which is nearly insoluble in water; it dissolves in alcohol with a reddish-yellow colour without showing fluorescence. Tetrabromfluoresceïn is a fairly strong acid, and its salts are not decomposed by acetic acid. The aqueous solution of eosin becomes darker on addition of caustic soda, and produces a soluble yellowish-red precipitate. The

solution in strong sulphuric acid is yellow, and yields, on diluting with water, a yellow flocculent precipitate.

Eosin dyes a more yellowish shade than any of the following eosins or rhodamines. The colour is a yellowish-pink, or, in conjunction with lead mordants, a cherry-red.

ERYTHRIN. $C_{20}H_6Br_4O_3(OCH_3)(OK)$.

Eosin, soluble in spirit; Primerose à l'alcool; Methyleosin.

Erythrin is the methyl-ether of eosin, and is produced by heating eosin with wood spirit and sulphuric acid.

Dark red powder with a green reflex, sparingly soluble in water, not soluble in absolute alcohol, but freely soluble in alcohol containing 50 per cent. water. This solution is red with a brownish-yellow fluorescence. HCl produces in the aqueous solution a brown-yellow precipitate; $NaOH$ makes the aqueous solution darker; solution in H_2SO_4 , yellow; on addition of water, brown-yellow precipitate.

Erythrin dyes a pink shade with a brick-red fluorescence, which is more bluish and brilliant than eosin. The colouring matter is added to the dye-bath in alcoholic solution, and its application is restricted to silk.

PRIMROSE. $C_{20}H_6Br_4O_3(OC_2H_5)(OK)$.

Primerose à l'alcool; Eosin, soluble in spirit; Eosin S; Eosin B B. Ethyleosin; Rose J B à l'alcool.

Primrose is the ethyl-ether of eosin, and is obtained by ethylating eosin. It forms a brown powder and closely resembles erythrin (methyleosin). The shade is more bluish.

ERYTHROSIN G. $C_{20}H_8O_3I_2(OK)_2$ or $C \left\{ \begin{array}{l} C_6H_2I-O K \\ C_6H_2I-O K \\ C_6H_4COO \end{array} \right.$

Dianthin G; Pyrosin J; Jaune d'orient. Iodoeosin.

Erythrosin G is an alkaline salt of diiodofluorescein, produced by the action of iodine on fluorescein.

Brownish powder; aqueous solution, red, without showing a fluorescence; HCl , brown-yellow precipitate; $NaOH$, soluble red precipitate; solution in H_2SO_4 , yellow; on diluting, brown-yellow precipitate.

Erythrosin G closely resembles the following dyestuff; but it possesses a more yellowish shade.

ERYTHROSIN. $C_{20}H_6O_3I_4(ONa)_2$.

Eosin, bluish; Eosin B; Eosin J; Primrose, soluble; Dianthin B; Pyrosin B; Erythrosin B; Iodoeosin B; Rose B à l'eau.

Erythrosin is an alkaline salt of tetraiodofluorescein, and is obtained analogously to eosin.

Brown powder; aqueous solution, cherry-red, without fluorescence; H Cl, orange flaky precipitate; Na O H, soluble red precipitate; solution in H₂ S O₄, yellow; on diluting, brown-yellow precipitate.

Erythrosin dyes a very bright bluish-red, similar to primrose, but richer in tinctorial powers.

EOSIN B N or SAFROSIN. C₂₀ H₆ O₃ Br₂ (N O₂)₂ (O K)₂.

Eosin-scarlet; Methyleosin; Ecarlate.

Eosin B N or safrosin is the potassium salt of dibromdinitrofluorescein, and is obtained by the action of nitric acid and bromine on fluorescein.

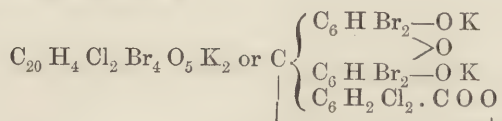
Dark olive-brown powder; aqueous solution, yellowish-red, with a faint dark green fluorescence; H Cl, yellow precipitate; Na O H, no change; solution in H₂ S O₄, yellow; on diluting, yellow precipitate.

Safrosin dyes a bluish-red shade similar to erythrosin, but less bright. It is more suitable for wool than for silk dyeing, and is somewhat faster to light and milling than most of the other eosins. Various mixtures of eosin B N with other dyestuffs are brought into the market, and have been used quite extensively in wool dyeing.

Lutecienne is a mixture of salts of tetranitrofluorescein, dinitrofluorescein and orange II.

Nopalin, Imperial Red, and Coccin are similar mixtures, containing dinitronaphthol (naphthol-yellow) and aurantia.

PHLOXIN or PHLOXIN P.



Phloxin is an alkaline salt of tetrabromdichlorfluorescein, and is produced by the action of bromine on dichlorphthalic anhydride.

Brownish-yellow powder; aqueous solution, red, with a yellowish-green fluorescence; H Cl, orange-yellow precipitate; Na O H, no change; solution in H₂ S O₄, yellow; on diluting, reddish precipitate.

Phloxin dyes a beautiful bluish-red shade, bluer than erythrosin.

CYANOSIN. C₂₀ H₄ Cl₂ Br₄ O₃ (O C H₃) (O K).

Cyanosin or methylphloxin is produced by methylating phloxin.

Brownish-red powder, sparingly soluble in water, freely soluble in dilute alcohol with a crimson colour, and a reddish-yellow fluorescence; H Cl, destroys the fluorescence of this solution; Na O H, has no action; solution in H₂ S O₄, yellow; on diluting, yellowish-red precipitate.

Cyanosin dyes a much brighter and bluer shade than phloxin.

phthalic anhydride or by the action of diethylamine on the chloride of fluorescein.

Red-brown or bluish-red or greenish crystalline powder; aqueous solution, magenta-red with a brownish-yellow fluorescence; the fluorescence of the aqueous solution disappears on boiling, but reappears when the liquid is allowed to cool; H Cl makes the solution more yellowish; Na O H precipitates the colour-base in the form of pink-coloured flakes; solution in $\text{H}_2\text{S O}_4$, brownish-yellow, with a strong green fluorescence; on diluting, crimson.

Application (see also p. 558).—**Cotton** is not dyed extensively with rhodamine B, since the colour is not very fast on this fibre. The usual methods which are employed for the dyeing of the basic colours are applicable for rhodamine. A light bluish-pink is obtained on unmordanted cotton, a fluorescent bluish-pink on cotton which has been prepared with Turkey-red oil and alumina, and a dull very bluish-red without fluorescence on tannin and antimony mordants. Rhodamine is used with advantage for topping and brightening alizarin-red on oiled goods; but small quantities only must be used, lest the shade become too bluish and of lessened brilliancy.

Wool and silk are dyed, as with the eosins, in slightly acid baths, silk in acidulated boiled-off liquor. Exceedingly bright bluish-pink shades with a red fluorescence are produced, which are valuable on account of their greater fastness to light than other colours of this class.

Rhodamine B dyes very evenly on wool, and the shades obtained are quite fast to soaping, but the colour is liable to bleed into the white on milling. Beautiful, pure and bright red colours are produced on wool by mixtures of rhodamine with the azo-oranges and azo-scarlets.

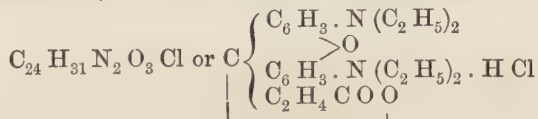
RHODAMINE G (B. A. S. F.)

The composition of this substance has not yet been made known.

Red-brown powder; aqueous solution, magenta-red with a brownish-yellow fluorescence, which diminishes on heating; H Cl, makes the solution more yellowish; Na O H precipitates the colour-base in the form of red flakes; solution in $\text{H}_2\text{S O}_4$, yellow, with an intense green fluorescence; on diluting, red.

Rhodamine G resembles rhodamine B, and is applied in a similar way to the textile fibres; it dyes a slightly yellower shade of pink.

RHODAMINE S (B. A. S. F.; Bayer; Bindschedler).



Rhodamine S is the basic hydrochloride of the succinein of

diethylmetamidophenol, and is obtained analogously to rhodamine B by heating succinic anhydride $C_2H_4 \begin{smallmatrix} CO \\ CO \end{smallmatrix} O$ with diethylmetamidophenol. It is similar to rhodamine B.

Blackish-brown powder; aqueous solution, magenta-red, with a brownish fluorescence which disappears on heating; HCl , makes the solution more yellowish; $NaOH$, precipitates the colour-base as crimson flakes; solution in H_2SO_4 , brownish, with a very strong green fluorescence; on diluting, red solution.

Application.—Rhodamine S is applied like rhodamine B. It possesses greater affinity for unmordanted cotton, and is suitable for dyeing cotton, and cotton and silk mixed goods without the aid of mordants. It dyes a slightly yellower pink than rhodamine B and G.

The dye-bath is prepared with the colour solution, and 1 or 2 parts of acetic acid for 1,000 parts of water. The material is worked in this bath until the desired shade is obtained. For cotton the temperature is raised to 35° to 45° ; mixed goods are dyed without heating.

YELLOW CORALLIN (AURIN AND ROSOLIC ACID).

This substance is prepared by heating phenol with dehydrated oxalic acid and sulphuric acid to 120° or 130° . It is a mixture of *aurin* ($C_{19}H_{14}O_3$), *methylaurin* ($C_{20}H_{16}O_3$), and *corallinphthalin* or *pseudorosolic acid* ($C_{20}H_{16}O_4$).

Aurin is constituted analogously to pararosaniline (and methylaurin to rosaniline); while corallinphthalin is the leuco-compound of a phthalein. Indeed it is not a colouring matter itself, but is converted into one by oxidation.

Yellow corallin forms irregular lumps with a green metallic lustre or a red-brown powder. It is either insoluble in water or soluble with a red colour (sodium salt). The aqueous solution is coloured yellow by hydrochloric acid and yields a brownish-yellow precipitate; caustic soda has no action. The solution in sulphuric acid is yellow. Yellow corallin dissolves in alcohol with a yellow colour, which is not affected by hydrochloric acid, but becomes cherry-red on addition of caustic soda. The change of colour is very sharp, and corallin is, therefore, used as an indicator for alkalies; it is not suitable for ammonia.

Application.—Corallin is seldom employed in dyeing, owing to its extreme fugitiveness to light, soap, and acids. It is still used by calico- and woollen-printers. Wool and silk may be dyed in a weak soap-bath, heating it gradually to the boiling-point; the silk is brightened with acetic acid.

RED CORALLIN. PEONY-RED. AURIN R.

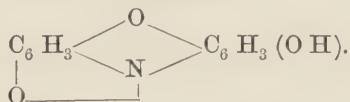
This dyestuff is produced by the action of ammonia on yellow corallin. It is either an intermediate compound between yellow corallin and magenta or a salt of both substances (rosolate of magenta).

It resembles in its properties and applications yellow corallin, and dyes a yellowish red.

RESORCIN-BLUE (FLUORESCENT BLUE) (Bindschedler ; Kern).



Resorcin-blue is the ammonium compound of tetrabromoresorufin which is obtained by treating resorufin in alkaline solution with bromine. Resorufin ($\text{C}_{12} \text{H}_7 \text{N O}_3$) is obtained by the action of nitrous acid on resorcin, and is thus constituted :—



Resorcin-blue comes into commerce as an olive-brown liquid which contains small green crystals. The mass dissolves in water with a violet colour; hydrochloric acid produces a brownish precipitate; caustic soda forms a red-violet precipitate, while the solution becomes red-violet with a brownish-yellow fluorescence. The dry substance dissolves in sulphuric acid with a blue-violet colour, which becomes, on diluting with water, at first red-violet and then a brown-orange precipitate is separated out.

Application.—Resorcin-blue is not dyed on cotton. It is little used for wool dyeing, but is employed on silk. It dyes this fibre with a blue-violet colour and a remarkable reddish fluorescence which shows itself very prominently by gaslight; when used in combination with other colouring matters it gives pleasing shades, all possessing fluorescence. The shade is very fast to light, washing, and acids.

Silk is dyed in a boiled-off liquor bath which has been slightly acidulated with acetic acid, and is brightened with acetic, tartaric, or sulphuric acid.

MORDANT-COLOURS.

Artificial Dyestuffs which are fixed on the Textile Fibres with the aid of Metallic Mordants.

This chapter comprises a great variety of artificial dyestuffs which differ from the preceding colouring matters by the common property of dyeing the vegetable and animal fibres in conjunction with metallic mordants only. The most important of these dyestuffs, alizarin, is also met with in the vegetable kingdom, and has been mentioned under "madder" in the chapter on the natural dyestuffs. It is distinguished by the property of yielding with different mordants different colours, which are distinguished by extraordinary fastness to light, soap, milling, and other influences.

Several derivatives of alizarin are applied in dyeing in the same way as alizarin, and are distinguished by a similar resistance to colour-

destroying agents. These colouring matters, like alizarin-orange or alizarin-blue, have been justly called "alizarin-colours;" but the name has been extended to several dyestuffs which are not at all chemically related to alizarin—*e.g.*, alizarin-yellows and alizarin-black, and only deserve the name because they are dyed by the same methods as the true alizarin-colours and can be dyed along with them in one bath. Recently, however, a very considerable number of dyestuffs have been introduced which share the property of dyeing on metallic mordants with the alizarins (and are, as a rule, also very fast to the various agents). It does not appear appropriate to name all these colours "alizarin-colours," nor to separate the new additions from the older products, since they are very similar in their application and are frequently mixed in the dye-bath; hence we follow the recommendation of R. Nietzki,* and classify all these dyestuffs as "mordant-colours." The common characteristic property of these dyestuffs is their ability to form insoluble colour-lakes with metallic oxides, which can be fixed on the textile fibres; but beyond this fact they differ greatly. Some cannot be dyed at all without mordants and cannot be considered as true colours, but as colouring principles which yield the coloured body only in combination with metallic oxides. Of these substances some produce with the different oxides *one* colour, or at most various shades of *one* colour; others yield a great variety of colours, notably alizarin. It does not seem, however, possible to base a practical classification on this phenomenon. Other colouring matters are more or less capable of dyeing the textile fibres without mordants—*e.g.*, alizarin-blue, alizarin-yellow GG, and cloth-red; but this property also seems to be unsuitable as a basis for a division into several groups. Hence, the grouping which will be adopted here is that depending on their origin, not on the distinguishing character, of the different mordant-colours.

(a) *Alizarins.*

Alizarin (Alizarin, blue shade).	Alizarin-Cyanin G.
Isopurpurin, (Alizarin, yellow shade).	Alizarin-Maroon.
Flavopurpurin („ „)	Alizarin-Orange.
Alizarin S (2 S and 3 S).	Alizarin-Blue.
Purpurin.	Alizarin-Blue S.
Anthracene-Brown.	Alizarin-Green S.
Alizarin-Bordeaux.	Alizarin-Indigo-Blue S.
Alizarin-Cyanin R.	Coerulein (Coerulein S).

(b) *Derivatives of Pyrogallol.*

Gallein.	Prune.
Gallocyanin.	Gallamine-Blue.
Gallanilid-Blue.	Galloflavin.
Gallanil-Violet BS.	Alizarin-Yellow A.
Delphin-Blue, or Crumpsal Fast Blue.	Alizarin-Yellow C.

* *Journ. Soc. Dyers and Col.*, 1889, p. 161.

(c) *Various Phenolic Compounds.*

Azarin S.
Azarin R.

Aurotin.
Alizarin-Black S.

(d) *Azo-compounds.*

Cloth-Red G (Oehler).
Cloth-Red B "
Cloth-Red B (Bayer).
Cloth-Red 3 G "
Cloth-Red G "
Clayton Cloth-Red.
Cloth-Orange.
Cloth-Brown.
Cloth-Brown, yellowish.
Alizarin-Yellow G G.

Alizarin-Yellow R
Terra-cotta R.
Milling-Yellow (Dahl).
Diamond-Yellow G.
Diamond-Yellow R.
Patent Fustin.
Azo-Green.
Diamond-Green.
Diamond-Black.
Chromotrops (see p. 536).

(e) *Nitroso-compounds.*

Dinitroso-Resorcin.
Essain.
Dinitroso-Naphthols.

Dioxin.
Naphthol-Green.

The first group, comprising the alizarins, contains the double ketone-group $\left\{ \begin{smallmatrix} \text{C O} \\ \text{C O} \end{smallmatrix} \right\}$ as chromophor, and as auxochromous groups two hydroxyls in orthoposition to each other, and one of them in orthoposition to one of the groups C O. (See *Alizarin*.)

The second group consists of derivatives of pyrogallol (or gallic acid), they also contain two or more hydroxyls in orthoposition to each other, and presumably one of them also in orthoposition to the chromophor. Coerulein may also be numbered among the members of this group.

The third group consists of several substances which have little in common, and the chemical reactions which take place in dyeing with them are also different.

The fourth group consists of azo-compounds, which are either derivatives of salicylic acid, or of naphthol sulphonic acids, or of substances of unknown constitution (patent fustin).

The fifth and last group is formed by five nitroso-compounds of analogous constitution. These substances differ chemically and tinctorially from the preceding colours, and we refer to the paragraph describing them specially.

The mordant-colours are used in the dyeing and printing of cotton, linen, wool, and silk, and are used in constantly increasing quantities on account of the great fastness they possess to soaping and milling. As a rule, they are very fast to light and resist well most of the other agents, such as sulphur dioxide, chlorine, acids, or alkalies—in short, they belong to the fastest colours known. It may be noticed that most of the natural colouring matters which are distinguished by

fastness are also mordant-colours—*e.g.*, logwood and fustic. Indigo in common with some artificial dyestuffs, such as indophenol and aniline-black, makes an exception to the rule that it is only the mordant-colours which possess extraordinary fastness. Indigo, aniline-black, &c., however, have an analogy with the mordant-colours, inasmuch as they are produced in the fibre only in their ultimate form, by a chemical reaction whereby insoluble compounds are produced which possess considerable resistance and inactivity towards most chemical agents.

Methods of Dyeing with the Mordant-Colours.—The dyeing with the mordant-colours takes place, as a rule, in two phases:—(1) *Mordanting*; (2) *Dyeing (mordanting and dyeing method)*. Both operations may, in some cases, be done together in one bath by the *single-bath method*; sometimes their order is inverted by first dyeing or “*stuffing*,” and subsequently fixing or “*saddening*” with the mordant (*dyeing and saddening method*).

The various sesquioxides, principally those of aluminium, chromium, and iron, and, in addition, stannous and stannic oxide, are used as mordants; the other oxides are of minor importance. Chromic oxide is the mordant employed with the greatest number of these colours, while aluminium oxide yields the most brilliant shades, for example, “Turkey-red.” The principal mordant for the nitroso-compounds is ferric oxide; for other colours it is not frequently used, except for the production of very fast shades of violet with the aid of alizarin.

Most of the mordant-colours can be mixed and dyed from the same bath, provided that they are fixed by the same mordant; colours requiring different mordants cannot be used with advantage for the production of mixed shades in one bath.

The colour-lakes frequently behave as mordants towards the basic colours, which latter are sometimes used to brighten or to shade a mordant-colour, either by adding the basic colour to the dye-bath or by topping afterwards.

The mordant-colours, which are readily soluble in water and are sold in form of powders, are added to the dye-bath in the dissolved state. They require 20 to 50 times their own weight of water; the solutions are filtered before being used. With the exception of the bisulphite compounds, they may be dissolved in boiling water. The latter, however, are decomposed by hot water, so that the water should be cold, or, at most, lukewarm. Many of the mordant-colours are sold as sparingly soluble pastes; these are mixed with some water and passed through a fine sieve into the dye-bath; they are thus in a state of fine division and gradually dissolve in the dye-liquor. These pastes require care in storing; they should be kept in well-covered casks in a place where they are protected from frost and not liable to dry up; if not perfectly closed the casks should be covered with a damp cloth (which has been saturated with glycerin). Before taking out any paste from

a cask it should be well stirred up with a wooden stirrer until the whole is of a uniform consistency.

The paste loses in colouring power if it dries up, since it thereby becomes less soluble in the dye-bath. The best method of restoring its former quality is to dissolve the substance in caustic soda, precipitate the colouring matter with a slight excess of sulphuric acid, wash the precipitate with water, and dilute the resulting paste with a sufficient quantity of water. This well-known method has been the subject of a recent patent for producing dry alizarin as a commercial article, which may be converted in the dye-house into the paste form.

Dyeing of Cotton with the Mordant-Colours.—Cotton is always dyed with these products by the separate "mordanting and dyeing method." Aluminium, chromium, and iron mordants are principally used; their application has been described in the chapter on mordants (Part V.). Some special methods, notably the production of Turkey-red, will be described with the dyestuffs.

Dyeing on Aluminium Mordants (see p. 232).—These mordants are used for alizarin, alizarin-orange, alizarin-maroon, alizarin-bordeaux, anthracene-brown, and coerulein. The methods of dyeing are described in connection with the dyestuffs themselves.

Dyeing on Chromium Mordants (see p. 256).—The lack of a thoroughly satisfactory mordant, especially for yarn dyeing, has restricted to some extent the fixing of these colours on cotton by chromium; but during the last few years various good methods have been invented, and are largely used. The beautiful mode colours in summer dresses, now so frequently seen, owe their existence to the new art of cotton dyeing by first fixing chromic oxide as a mordant, then preparing a white or coloured pattern by discharge-printing, and finally dyeing with a mordant-colour.

It is not essential that the goods should be prepared with oil before mordanting; but the oil is a valuable fixing agent for the mordant, and, in addition, it gives a better appearance and greater fastness to the colour. Once saturating the cotton with oil (1 volume of neutralised Turkey-red oil (50 per cent.) diluted with 9 volumes of water) and subsequent drying, is sufficient. After the oiling, if necessary, impregnating with tannin—for instance, steeping in a hot solution of 1 part of sumach extract (53° Tw.) in 100 of water for 12 hours—follows, in some cases. The methods for mordanting cotton with chromic oxide have been described in the chapter on mordants; for yarn in hanks, basic chromium chloride, chromium acetate, and chromium mordant G A I. are the most suitable; for loose cotton, cops, or piece goods, in addition to these Koechlin's alkaline chrome mordant, and chromium mordant G A II. are useful; Koechlin's mordant appears to be the best which has been recommended as yet. The new method of producing a double chromium-zinc mordant with sodium zincate (see *Gallocyanin*, p. 624) will, no doubt, prove valuable

in many cases. If it is desired to use a mixed aluminium and chromium mordant, it is best to fix first the necessary quantity of chromic oxide, and subsequently the alumina; the latter being fixed more easily than the former.

The mordanted goods are well washed in water to remove any loosely adhering mordant, which might cause the ultimate colour to rub and smear off. The goods are dyed immediately without drying. The water is slightly acidulated by the addition of acetic acid; in the case of soft water, 1 part of acid is added for 1,000 parts of water, but for alkaline water more is used; a great excess of acid is injurious. Frequently some Turkey-red oil (2 parts of oil for 1,000 parts of water) is added, to give the colour brightness. The colour is added to the dye-liquor, the goods are introduced into the cold bath, the temperature is raised in about one hour to the boiling point, and maintained thus for one to two hours. After the dyeing the goods are soaped at 60° or at the boil, rinsed in water, and dried.

Dyeing on Iron, Tin, and other Mordants.—The general application of these mordants has been given in the chapter on mordants. They are used in special cases only and their employment will be described in connection with the dyestuffs for which they are required. The iron mordants are important for the fixation of the nitroso-compounds.

Jute is not dyed with the mordant-colours, since the process of applying them is too expensive for this material.

Dyeing of Wool with the Mordant-Colours.—The use of natural mordant dyestuffs, *e.g.*, logwood, fustic, or madder, in wool-dyeing dates from a very early period, and the employment of the principal wool-mordant, viz., potassium bichromate, was introduced about half a century ago. The application of artificial mordant-colours in wool dyeing, however, has only become general during the last decade. During the last 15 years the methods of dyeing have been greatly improved, and it is now possible to produce a wide range of colours on wool, which are equal in fastness to any hitherto obtained, with the possible exception of indigo. J. J. Hummel directed, in an admirable paper read in 1884 before the Society of Dyers and Colourists,* the attention of wool dyers to the valuable properties of the alizarin dyestuffs, and it is largely owing to his endeavours that the artificial mordant-colours have so rapidly found a general application in British dye-houses. The merits of the mordant-colours, especially of the true alizarins, consist (1) in their extraordinary fastness to air and light, to dilute acids and alkalies, to milling, scouring, carbonising, and stoving—the smearing-off, or rubbing, which was formerly very objectionable, has been overcome to a great extent (see below); (2) in the fact that the wool does not lose its softness and spinning properties; in this respect the artificial mordant-colours are, as a rule, preferable to the wood-colours. The competition

* *Journ. Soc. Dyers and Col.*, 1884-85, p. 11.

of the two is chiefly a matter of price, and the cost of the former prevents their use to a great extent.

The principal factor for the successful dyeing of wool with these colours is the thorough purification of the fibre from fatty and greasy matters. Unless these are removed, they form with the mordants sticky soaps which loosely adhere to the wool and attract dyestuff; but as they form no intimate combination with the fibre, they are always disposed to rub off, and to soil other yarns they come in contact with in milling. It is most essential that the loose wool should be thoroughly scoured before it is spun, since it is almost impossible to remove "yolk" from the yarn; the difficulties frequently met with in yarn dyeing are often owing to the fact that the wool from which it is spun has not been sufficiently scoured.

Mordanting.—The same metallic mordants as are used on cotton are also used on wool for dyeing with the mordant-colours—viz., aluminium, chromium, iron, and tin in conjunction with, or without, calcium; all of these are employed more or less for alizarin, but chiefly aluminium and chromium, especially the latter. Most of the other dyestuffs are fixed on chromium mordants only. The form, however, in which these metals are used in wool dyeing is different from that of those used for cotton, and no olive oil or Turkey-red oil is employed in wool dyeing.

Dyeing on Aluminium Mordant (see p. 236).—Only the several alizarin-reds, alizarin-maroon, and alizarin-orange are fixed on wool with the aid of aluminium. (See pp. 608 and 616.)

Dyeing on Chromium Mordants (see p. 260).

(a) *Mordanting and Dyeing Method.*—The method most generally applied is boiling the wool with 3 to 4 per cent. of potassium bichromate (or sodium bichromate) with, or without, the addition of 1 per cent. of sulphuric acid. The best results are obtained by mordanting with 3 per cent. of bichromate and $2\frac{1}{2}$ per cent. of tartar; but on account of the high price of the tartar comparatively little use is made of it. Recently chromium fluoride has been introduced.

The well-scoured and wetted-out wool is boiled for 1 to 2 hours in the mordanting liquor containing the required amount of bichromate with, or without, sulphuric acid or tartar; about 2 to 4 per cent. of chromium fluoride with half its weight of oxalic acid are used in the same way. The wool when taken out of the mordanting bath is allowed to lie overnight, the next day it is well washed in water and dyed. A passing of the wool through a dilute solution of sodium bisulphite (see p. 262) before the washing, is beneficial in many cases, in others it is not advisable. The mordanted goods should be kept in the shade in order to prevent a partial decomposition of the mordant by strong light and subsequent uneven dyeing.

The dye-liquor is first prepared with acetic acid in the proportion of about 1 part per 1,000 parts of water; the more alkaline the water the more acetic acid is required; the water should have a distinctly

acid reaction. The colouring matter is then dissolved or mixed with the acidified water taken from the dye-bath, and $\frac{1}{3}$ to $\frac{1}{2}$ of it is added to the dye-bath (in the case of insoluble pastes through a fine sieve). The material is entered into the dye-liquor at a low temperature, in order to ensure even and regular dyeing; the temperature should not be higher than 50° for dark shades, or 30° for light shades. After working some time in the bath the rest of the colour is gradually added. The temperature is slowly raised to boiling; but during the first hour 60° should not be exceeded—in dyeing with Obermayer's machine 50° —and the boiling point must not be reached before the dye-liquor is almost decolorised; 1 to $1\frac{1}{2}$ hours boiling are required to develop and thoroughly fix the colour. Any further addition of colouring matter to the dye-bath, either to deepen or modify the shade, should only be made after cooling the dye-liquor down to 30° or 50° with cold water containing the requisite amount of acetic acid. If a considerable quantity of the dyestuff has to be put in, it should be added in several small portions at short intervals.

To dye piece goods, yarns, and slubbing through and evenly, especially thick milled cloths, or lighter shades and "modes," the Badische Anilin und Soda Fabrik recommends the following method of dyeing:—Heat the water not above 40° , and add per 1,000 parts of water 3 parts (by volume) of ammonium acetate,* and the required amount of dyestuff dissolved or mixed with warm water. Enter the goods and turn frequently, especially for the first 15 minutes; raise in about 45 minutes to boiling, and boil for 30 minutes more. For every 1,000 parts of dye-liquor add then 3 parts of acetic acid, divided into 3 parts; shut the steam off, lift the goods on each addition, and turn them frequently. Two hours more boiling fixes the colour thoroughly. For shading, the bath need not be cooled down, but the free acetic acid should be neutralised with ammonia; about 1 to $1\frac{1}{2}$ parts of ammonia per 1,000 parts of liquor are required; an excess must be avoided.

The artificial mordant-colours can be used for dyeing in the same bath with each other, and with logwood, fustic, &c.; they can be saddened with copperas and brightened with indigo-carmin and almost any of the aniline colours.

(b) *Single-bath Method.*—A number of mordant-colours which are not chemically changed by the oxidising action of chromic acid, notably alizarin and most of the azo-compounds of this group (e.g., alizarin-yellow G G), yield excellent shades in one bath, which are as full as those obtained by the mordanting and dyeing method, and almost equally fast to milling. Three per cent. of bichromate and in some cases as much sulphuric acid are used; in order to ensure even and regular dyeing it is necessary to work for some time in the cold, then raise the temperature gradually to boiling and keep at the

* The ammonium acetate is prepared by adding so much acetic acid to commercial ammonia water as will cause the mixture to give a very slightly acid reaction.

boil for some time. Chromium fluoride is still better adapted for the "single-bath method" than bichrome, because it does not easily affect the colouring matters.

For *Dyeing with other Mordants*, see *Alizarin and Nitroso-compounds*.

Dyeing of Silk with the Mordant-Colours.—These colouring matters are not used very extensively on silk, because their fixation with the aid of mordants is much more expensive than that of the substantive dyestuffs, and the latter are as a rule fast enough for the requirements of silk dyeing, and yield more brilliant and purer shades. Besides, the mordant deposited in the fibre causes the silk to lose some of its lustre and pliability.

The following instructions are, in the main, those of the Badische Anilin und Soda Fabrik :—

The silk is discharged, washed and wrung out, and then mordanted with aluminium or chromium salts (see pp. 239 and 264).

Dyeing with Aluminium Mordants.—Make a solution containing 60 grms. (10 oz.) of alum and 6 grms. (1 oz.) of soda crystals in each litre (or gall.) of water, and heat until the precipitate which is formed by the reaction has redissolved. Enter the silk, and turn from 10 to 15 minutes, then immerse it completely into the bath, and let it remain there for 12 hours. The bath can be used again after being freshened up with alum and soda crystals. Aluminium acetate or nitro-acetate (10 to 15° Tw.) may be used; $\frac{1}{2}$ per cent. of tin crystals (of the quantity of the mordanting preparation) may be added.

After mordanting, wring the silk well out, and work for 15 minutes in a cold bath of silicate of soda ($\frac{1}{2}$ ° Tw.), wring, wash very well, wring again, and dye without drying. (See below.)

Another method, which gives excellent results,* is to prepare a bath with 1,000 grms. (10 lbs.) of alum, and 400 grms. (4 lbs.) of sodium-hyposulphite per 10 litres (10 galls.) of water, and to soak the silk in this liquor 3 hours; heat during the first hour to 40°, in the second to 60°, and in the third to 80°; wash and dye. (See below.)

Dyeing on Chromium Mordants.—For darker shades the use of chromium mordants is preferable. The silk, after discharging and washing, is immersed for 6 hours in a solution of chromium chloride (52° Tw.), and then treated, as by the method given for aluminium mordants, with silicate of soda, &c. The Hoechst Farbwerke recommend using their chromium mordant G A III. diluted with four times its volume of water, steeping the silk in this liquor for 12 to 24 hours, and then simply washing without fixing.

Dyeing on Iron Mordant.—Steep in basic nitrate of iron over night, wring, wash, and soap in boiling soap solution. (See p. 270.)

Dyeing.—The dye-bath should contain per 100 litres (galls.) 20 litres (galls.) of boiled-off liquor. The latter should be free from soda, and neither too old nor too slimy—*i.e.*, it should not contain too much

* H. Lange, *Faerberzeitung*, 1889, p. 90.

gum. The liquor obtained from the second boiling-off is used with advantage.

The amount of dye-liquor should be 20 to 30 times the weight of the silk; for an aluminium mordant it is neutralised with acetic acid; for a chromium mordant it is slightly acidified. The colour is added before the acid, the silk is entered as soon as the acid has been put into the bath, and worked cold for 15 minutes; during 45 minutes the bath is heated to boiling, and kept at this temperature for one hour more. The silk is then well washed in water and soaped for 15 minutes in boiling soap solution 2 grms. per litre ($\frac{1}{3}$ oz. per gall.); strong and prolonged soaping increases the brilliancy of the colours. Finally it is worked for brightening in tepid water, containing 25 grms. of acetic acid per litre (4 oz. per gall.), and dried without washing.

The mordant- and dye-baths may be used continuously.

The mordant-colours are, as a rule, very fast to light, soap, or milling, if properly dyed, on silk. The affinity of the silk fibre, however, for the metallic mordants, especially for chromic oxide, is less distinct than that of wool; and the colours are not always fixed quite so fast on silk as on wool. Still the colours are much faster on silk than the acid or basic aniline-colours and deserve the attention of silk-dyers.

ALIZARIN AND DERIVATIVES OF ALIZARIN.

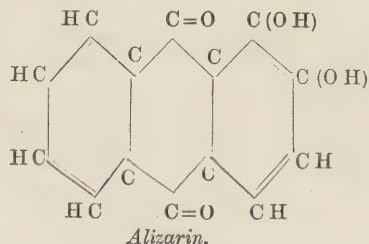
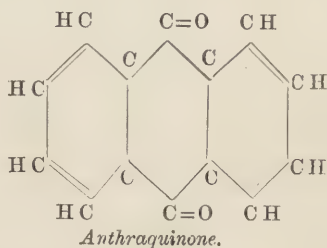
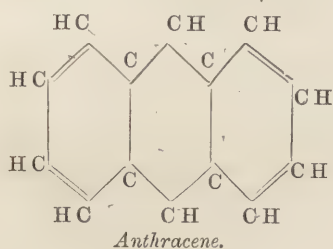
History and Chemistry of Alizarin.—According to the reports of Pliny, Dioscorides, and Strabo, madder-root was used for dyeing by the ancients. In eastern Europe this use has been continued ever since.

In western Europe it disappeared from commerce for many centuries, and as late as 1507 its culture was reintroduced into Silesia and about the same time into the Netherlands. It is only within the last century that madder has been cultivated in France, where for some time its production has been fostered by the government.

The first systematic chemical examination of madder was made by Robiquet and Colin, who, in 1826, discovered therein two dye-stuffs, alizarin and purpurin, and determined their exact composition. Further important investigations were made by Runge, Gaultier de Claubry and Persoz, Debus, Schunck, Rochleder, Strecker, and others, by whom our knowledge of these colouring matters has been promoted. But the results of their researches were conflicting, and even the exact composition of alizarin and purpurin became doubtful in the course of time. In 1868 two young chemists, C. Graebe and C. Liebermann, succeeded in clearing the darkness, and not merely discovered the constitution of both compounds, but prepared them from anthracene, a hydrocarbon which is present in coal-tar. As the fruit of their studies the great alizarin-industry has been built up; the manufacture of other chemicals (*e.g.*, the bichromates and sulphuric anhydride) has been

encouraged and stimulated and their prices greatly reduced; and last, but not least, hundreds of thousands of acres which were used for the cultivation of madder have been made available for the production of the necessaries of life. Madder has almost completely disappeared from commerce because it could not compete with artificial alizarin in price, purity, concentration, and uniform quality of the colouring substance. In wool dyeing it is still used to a slight extent because it dyes more level than the artificial product; but even here it owes its employment more to the antiquated demands of the consumer than to its intrinsic merits. On the other hand, effects, especially in calico-printing, can be obtained with artificial alizarin which could not be produced at all with madder or madder extracts, while its lower cost has brought about a saving in time and expense.

Alizarin, so-called by Robiquet and Colin, after "Lizari," the trade-name of the Levantine madder-roots, is a derivative of the hydrocarbon anthracene ($C_{14}H_{10}$), or rather of the double-ketone of the latter, anthraquinone ($C_{14}H_8O_2$); alizarin is dioxyanthraquinone $C_{14}H_8O_4 = C_{14}H_6O_2(OH)_2$. The following formulæ explain the constitutions of these three important bodies:—

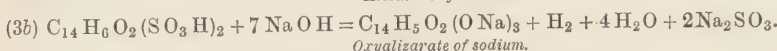
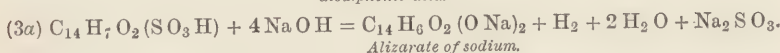
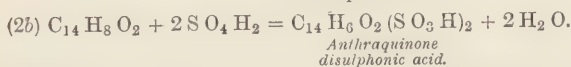
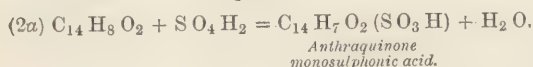
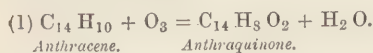


All true alizarin colours are derivatives of this dioxyanthraquinone. The isomeric substances which do not contain the hydroxyls in the same position (in orthoposition and next to one of the ketone groups, $C=O$) possess, according to Liebermann and Kostanecky, no tinctorial properties.

Alizarin is a phenolic substance, since it possesses hydroxyls connected with the benzene-nucleus. It evinces much stronger acidity than phenol or the naphthols, and acts as a dibasic acid; it decomposes sodium acetate on continued boiling, forming sodium alizarate and acetic acid (see below). It forms with metallic oxides permanent compounds,

the alizarates, which are (with the exception of those obtained with the alkalis) sparingly soluble or insoluble in water (colour lakes).

The manufacture of alizarin has been brought to a high state of perfection, almost the highest possible yield being realised. Anthracene is first oxidised with sodium bichromate and sulphuric acid, and the resulting anthraquinone is converted by very strong fuming sulphuric acid into sulphonic acids (monosulphonic, or alphasulphonic, or betadisulphonic acid of anthraquinone). The sulphonic acids are converted into alizarin or oxyalizarins by melting with caustic soda and a small amount of sodium chlorate; the melting is effected under high pressure in closed vessels.



The product of the anthraquinone alphasulphonic acid is called "flavopurpurin," while the name of that obtained from the anthraquinone betasulphonic acid is anthrapurpurin (or isopurpurin).

Both are constituted thus:— $(\text{H O}) \text{C}_6 \text{H}_3 \begin{smallmatrix} \text{C O} \\ \diagup \quad \diagdown \\ \text{C O} \end{smallmatrix} \text{C}_6 \text{H}_2 (\text{O H})_2$, while purpurin, another oxyalizarin, is $\text{C}_6 \text{H}_4 \begin{smallmatrix} \text{C O} \\ \diagup \quad \diagdown \\ \text{C O} \end{smallmatrix} \text{C}_6 \text{H} (\text{O H})_3$.

In the preceding equations it will be noticed that the anthraquinone sulphonic acids yield products which contain each time one hydroxyl group more than the number of sulpho-groups originally present. Thus the monosulphonic acid gives alizarin or dioxyanthraquinone; while from the disulphonic acids trioxyanthraquinones are obtained. The hydrogen which appears in these equations would act on the product and diminish the yield; to prevent this, chlorate of potash or soda is added to the melt (invention of J. J. Koch). The sodium compounds of the product are decomposed by acids, and the dyestuff, which is precipitated in a very finely divided flocculent state, is well washed and ground to a homogeneous paste containing a fixed percentage of pure dyestuff; most of the commercial alizarin now contains 20 per cent. of pure colouring matter.

The blue shade of alizarin only consists chiefly of true alizarin, *i.e.*, that dioxyanthraquinone which can be obtained from madder; alizarin V 1 new (B. A. S. F.) is chemically pure. The yellow shade of alizarin contains little alizarin, but more anthra- and flavopurpurin; both are very similar to alizarin, as also is purpurin, which is formed by heating

dry alizarin dissolved in sulphuric acid with manganese peroxide or with arsenic acid.

Alizarin (dioxyanthraquinone) in the pure state forms a reddish-yellow powder, or long resplendent bright orange-red needles. It melts at 289° to 290° C. It is almost insoluble in cold and very slightly soluble in boiling water, but it dissolves readily, with a reddish-yellow colour, in hot alcohol, ether, benzene, glycerin, glacial acetic acid, and similar solvents. In caustic soda it dissolves with a blue-violet, in ammonia with a purple colour; from these solutions it is precipitated by hydrochloric and other acids. In concentrated sulphuric acid alizarin dissolves with a brownish-red colour, and is precipitated from this solution by water without change; even hot sulphuric acid attacks alizarin but little, but by sulphuric anhydride it is converted into a sulphonc acid. By oxidation with manganese peroxide or arsenic acid it yields purpurin; when boiled with diluted nitric acid it gives phthalic and oxalic acids; fuming nitric acid forms nitropurpurin, and nitrous acid produces betanitroalizarin or alizarin-orange. Alkaline reducing agents decolorise it. It is converted by zinc dust and ammonia into colourless *desoxyalizarin*



other reducing agents produce different products. Alizarin is, generally, more stable than most other dyestuffs, and hence the colour has great fastness to light, and other agents.

Alizarin combines with metals forming salt-like compounds, either by combining in the free state with the hydroxides, or by the double decomposition of a soluble alizarate and a metallic salt. These lakes are but imperfectly known, as proved by the extended investigations of Liechti and Suida, which did not confirm the descriptions generally given. The lakes of the metals of the alkaline earths and of the heavy metals are insoluble, or sparingly soluble in water; the alkali- and ammonium-compounds of alizarin are readily soluble in water.

Liechti and Suida* have studied the calcium, aluminium, iron, and chromium lakes of alizarin, and have so fully explained the facts as attested by long practical experience, that a *résumé* of their results may follow here with advantage.

(1) *Calcium Alizarate*, $\text{C}_{14}\text{H}_6\text{O}_4\text{Ca}$, is obtained by the double decomposition of calcium acetate or chloride and ammonium alizarate as a purplish-black, sparingly soluble, crystalline body which is easily decomposed by acids (even by oleic acid). Alizarin, when treated with water containing bicarbonate of calcium, forms a precipitate of calcium alizarate, but only after some hours standing. Normal calcium carbonate scarcely produces any change, even after prolonged boiling with alizarin; but if aluminium hydrate is added a red lake is rapidly

* *Journ. Soc. Dyers and Col.*, 1885, p. 271; 1886, pp. 102, 120, 131, 146.

formed, carbon dioxide being evolved. Both acid and basic calcium alizarates are soluble in cold water and ammonia, but on heating the solutions normal calcium alizarate is rapidly formed. Normal calcium alizarate dissolves in clear lime water, with a ruby-red colour; if the solution is boiled for a short time it is decolorised and a red-brown precipitate is thrown down, consisting of a basic calcium alizarate, $C_{14}H_6O_4Ca + CaO$.

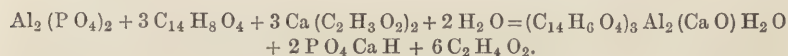
(2) *Aluminium Alizarates*.—In the absence of calcium salts alizarin in the free state does not, under any circumstances, combine with aluminium hydroxide. Normal aluminium alizarate, $(C_{14}H_6O_4)_3Al_2$, is best obtained by acting on a solution of ammoniacal alizarin with aluminium sulphate. It forms a purplish-black mass, which is soluble in pure water and in alcohol, especially on heating, also in ammonia without being chemically changed. If heated with water under pressure to $150^\circ C$. it is converted into a basic aluminium alizarate. An excess of alizarin prevents the precipitation of aluminium hydroxide from its salts by ammonia. The basic alizarates of aluminium are insoluble in water and alcohol, and the more basic they become the less soluble they are in ammonia.

(3) *Aluminium-calcium Alizarates*.—No less than ten compound alizarates containing different proportions of aluminium and calcium were prepared and analysed. They are insoluble in water, but partially soluble in ammonia. The quantity of calcium which enters into combination to form the lake increases in proportion with increasing quantities of alizarin employed; whereas, on the other hand, the quantity of alizarin entering into the combination depends upon the lime present therein. Most fabrics dyed with alizarin-red contain an excess of aluminium relatively to the alizarin and calcium; material mordanted with an unknown quantity of aluminium and subsequently dyed with alizarin and calcium acetate—as is done in practice—takes up calcium in the proportion of one atom of calcium to three molecules of alizarin. The most probable formula for the normal alizarin-red lake (before soaping) is $(C_{14}H_6O_4)_3Al_2(CaO), H_2O$. This lake is easily soluble in ammonia, and its ammoniacal solution can (like that of many others of these lakes) be mixed without change with Turkey-red oil. A lake of the composition $(C_{14}H_6O_4)_4Al_2Ca$ was found to be partially soluble in ammonia and had a tendency to form the normal alizarin-red lake. By a dye-trial it was shown that the normal lake could take up more alizarin; but this excess did not form an intimate combination and was removed by treatment with alkaline liquids (soaping). A lake, $(C_{14}H_6O_4)_5Al_2Ca_2$, described by Saget as being the fundamental compound of all alizarin-reds, is almost wholly soluble in water, and could not be produced under the conditions existing in the dye-bath; in place of it a basic lake is invariably formed. When treated with Turkey-red oil the aluminium-calcium lakes absorb oxy-fatty acids; the sulphuric acid liberated by the decomposition of the

oil partially decomposes the lake, and free alizarin as well as the sulphates of calcium and aluminium are formed. In all the ordinary alizarin- and Turkey-reds the operation of soaping disturbs the ratio of the calcium to the aluminium, some of the latter being removed. At the same time the lake absorbs some fatty acid from the soap.

Alkaline solutions of the normal alizarate and of the basic aluminium alizarate, $(C_{14}H_6O_4)_3(Al_2O_3H_3)_2$, are not changed when mixed with solutions of sodium phosphate, Turkey-red oil, soap, &c.; but on neutralising the liquids magnificent red lakes are thrown down.

Since in mordanting on the large scale the pure aluminium hydrate is very seldom produced on the fibre, but is usually fixed by means of silicate, arsenate, or phosphate of soda, Liechti and Suida considered it necessary to investigate the action of at least one of the compounds thus obtained, and aluminium phosphate was selected. Normal aluminium phosphate $(PO_4)_2Al_2$, prepared by precipitation and carefully washed, is not affected by alizarin; if, however, calcium acetate is added to the mixture, the formation of a lake ensues immediately. The filtrate has an acid reaction, and contains, besides acetic acid, a considerable quantity of phosphoric acid and calcium (most likely as acid calcium phosphate). This process is shown by the following equation:—



Aluminate of soda of the formula $Al_2O_3, 2Na_2O$, when acting on alizarin in aqueous solution in the proportion of $3 C_{14}H_6O_4$ to $1 Al_2O_3$, yields a red lake which easily dissolves in an excess of caustic soda or ammonia; aluminate of soda, of the formula $Al_2O_3, 3Na_2O$, yields a fine red solution which is not affected by lime water. Turkey-red oil or soap can be added to the solutions of the products of either aluminate with alizarin, without producing a change; but on adding calcium acetate a precipitate is formed. A solution containing alizarin, aluminate of soda, and calcium hydrate, printed on oiled material, gives a good steam-red.

(4) *Ferrous Alizarate*.—If solutions of ferrous sulphate and ammonium alizarate are mixed, a deep violet-black precipitate is at once produced which, after filtration and washing with water, is partly redissolved. This precipitate, when allowed to oxidise, probably forms a ferric-ferrous alizarate, $(C_{14}H_6O_4)_3Fe_2(FeO)$, which is constituted analogously to the above-described aluminium-calcium alizarate; it forms, when dried, a violet-black powder, having a bronzy lustre. Ferrous alizarate, freshly made, is easily dissolved by ammonia with a violet-black colour. It may be mixed with Turkey-red oil in this solution without undergoing any change. The alizarin here prevents the precipitation of ferrous or ferric hydrate by ammonia.

(5) *Ferric Alizarate*.—If a solution of ferric chloride is poured into

one of ammonium alizarate, providing the weights correspond to the equation—



a brownish-black precipitate is formed, which is slightly soluble in pure water, very easily soluble in ammonia with a violet colour, and may be mixed without change in this solution with Turkey-red oil. From this precipitate alizarin could be extracted by ether, while the residue contained one-half molecule of alizarin less than is required by the formula $\text{Fe}_2 (\text{C}_{14} \text{H}_6 \text{O}_4)_3$. A still more basic ferric alizarate was obtained by boiling freshly-precipitated ferric hydrate with alizarin suspended in water; the product contained about 2 molecules of alizarin to 3 molecules of ferric oxide.

Cotton-cloth mordanted with ferric oxide yielded, when dyed with alizarin in the absence of calcium compounds, only a very faint brownish-violet.

(6) *Ferric-calcium Alizarate*, $(\text{C}_{14} \text{H}_6 \text{O}_4)_3 \text{Fe}_2 (\text{Ca O}), \text{H}_2 \text{O}$.—Solutions of ferric chloride (1 mol.) containing different proportions (1, 2, or 3 mol.) of calcium acetate, were poured into solutions of ammonium alizarate (3 mol.). Also freshly-precipitated ferric hydrate (1 mol.) containing calcium acetate (1 mol.) was boiled with alizarin (3 mol.) suspended in water. In each case, a product having the composition $(\text{C}_{14} \text{H}_6 \text{O}_4)_3 \text{Fe}_2 (\text{Ca O}) \text{H}_2 \text{O}$ was obtained. The precipitate has a beautiful violet-black colour, and is partially soluble in ammonia. From the dye-trials executed in the same way and the analyses made, it further appears that this same product is the compound which forms the violet colour when alizarin is dyed on iron-mordanted materials. While materials mordanted with iron and dyed with alizarin in the absence of calcium gave only faint brownish-violet colours, those mordanted and dyed in the same way, except that the dye-bath contained increasing quantities (1, 2, or 3 mol.) of calcium acetate, yielded serviceable violet shades; the iron and calcium were found to be present in the proportion of equal molecules, and this ratio was not even altered when their absolute amounts were diminished by soaping. Thus, it cannot be doubted that the composition of alizarin-violet is $(\text{C}_{14} \text{H}_6 \text{O}_4)_3 \text{Fe}_2 (\text{Ca O}) \text{H}_2 \text{O}$ and that it is analogous to alizarin-red $(\text{C}_{14} \text{H}_6 \text{O}_4)_3 \text{Al}_2 (\text{Ca O}) \text{H}_2 \text{O}$.

(7) *Chromic Alizarates*.—The normal compound, $(\text{C}_{14} \text{H}_6 \text{O}_4)_3 \text{Cr}_2$, is obtained when chromium nitrate-acetate is treated with the corresponding amount of alizarin and an excess of ammonia, and the resulting violet solution is boiled till completely neutral. Normal chromic alizarate is a purple-violet substance, insoluble in water, but readily soluble in ammonia with a violet colour; this solution can be mixed with Turkey-red oil without change. Liechti and Suida did not succeed in producing a basic chromic alizarate, but they obtained an acid chromic alizarate corresponding to the formula

$\text{Cr}_2(\text{C}_{14}\text{H}_6\text{O}_4)_3 + 3(\text{C}_{14}\text{H}_8\text{O}_4)$ as a purple-red substance, easily soluble in water and in ammonia.

(8) *Chromic-calcium alizarate* was obtained by Liechti and Suida in a similar way as the normal chromic alizarate. If a solution of chromium nitrate-acetate, containing calcium acetate, is treated with ammonium alizarate, containing an excess of ammonia, a black-violet precipitate of calcium alizarate is formed. If the liquid, together with the precipitate, is boiled until the excess of ammonia has disappeared, the precipitate becomes more and more red-brown and the liquid colourless. The precipitate differs in composition according to the quantity of calcium acetate employed; if, for 3 molecules of alizarin and 1 molecule of chromium salt, 1 molecule of calcium acetate were used, a product represented by the formula $(\text{C}_{14}\text{H}_6\text{O}_4)_3\text{Cr}_2(\text{CaO})\text{H}_2\text{O}$ was obtained; if, however, more calcium acetate (*i.e.*, 2 and 3 molecules respectively) were employed for the same amounts of alizarin and chromium compounds, the ratio between alizarin and chromium in the resulting lake seems to remain unchanged, while the quantity of calcium entering into combination increases, but in such a way that the calcium present is not entirely taken up. Thus when 3 molecules of calcium acetate were used the ratio of alizarin, chromium, and calcium seemed to be 3 : 1 : 2. The precipitates are in each case insoluble in water, and the violet-brown colour approaches nearer to violet-black in proportion as the calcium is increased. These results were confirmed by dye-trials, which were made in the same way as those with ferric mordant. If the material was mordanted with chromium salt only and dyed without calcium being present, a faint puce only was obtained. If the experiment was regulated so that for 3 molecules of alizarin and 1 molecule of chromium salt 1 or 2 or 3 molecules of calcium acetate were present in the colour obtained, the molecules of chromium and calcium occurred in the following proportions:—

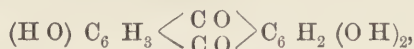
For 1 molecule of calcium acetate used,	Cr : Ca =	1 : 0.48
„ 2 „ „ „ „	Cr : Ca =	1 : 0.56
„ 3 „ „ „ „	Cr : Ca =	1 : 1.04

Samples which contain a colour composed after the ratio $3\text{C}_{14}\text{H}_8\text{O}_4 : \text{Cr}_2 : \frac{1}{2}\text{Ca}$ are of a darker puce shade than those produced in the absence of calcium, but they are not as dark as those containing a colour represented by the formula $(\text{C}_{14}\text{H}_6\text{O}_4)_3\text{Cr}_2\text{CaO}, \text{H}_2\text{O}$, which is obtained by using acetate of calcium in excess only. On soaping, the chromium-calcium-alizarin lake is much more altered in its composition than the corresponding iron lake.

These facts are in complete harmony with all practical experience; they also explain why the presence of lime in Turkey-red dyeing is absolutely necessary; why, in dyeing with chromium mordants, the presence of calcium salts may be dispensed with to some extent; and why different amounts of the latter give different results in dyeing with chrome- but not with alumina-mordant.

Alizarin S is the sodium monosulphonate of alizarin.

Isopurpurin or **Anthrapurpurin** or *oxyisoanthraflavic acid*,



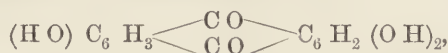
is obtained in the same way as alizarin, anthraquinone betadisulphonate of sodium being used instead of the monosulphonate. It closely resembles alizarin.

Isopurpurin crystallises from hot alcohol as orange needles, which melt above 300°C. It is almost insoluble in water, but freely soluble in hot alcohol. It dissolves in caustic alkalies, in ammonia, and in sodium carbonate with a violet colour, which is redder than that obtained with alizarin, but bluer than that from flavopurpurin. Isopurpurin dissolves in sulphuric acid with a brown colour, water precipitates it from this solution without change.

Isopurpurin yields more yellowish shades than alizarin, but less yellowish than flavopurpurin.

Alizarin 2 S is the sodium monosulphonate of isopurpurin.

Flavopurpurin or *oxyanthraflavic acid*,

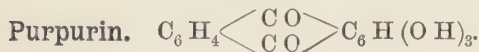


is isomeric with isopurpurin and is obtained, like this substance, when anthraquinone alphadisulphonic acid is melted with caustic soda by the alizarin process. It closely resembles alizarin and isopurpurin.

Flavopurpurin forms yellow needles, which melt above 330° and can be sublimated; it is almost insoluble in water, but readily soluble in cold alcohol and in hot glacial acetic acid. It dissolves in caustic soda with a purple colour, which is redder than those of the analogous solutions of alizarin and isopurpurin; in ammonia and in sodium carbonate flavopurpurin dissolves with a yellowish-red colour. The solution in sulphuric acid is red-violet; on diluting with water the dyestuff is precipitated without change.

The shades obtained with flavopurpurin are yellower than those obtained with alizarin or isopurpurin.

Alizarin 3 S is the sodium monosulphonate of flavopurpurin.



Purpurin was discovered by Robiquet and Colin along with alizarin in the madder roots. It was the first oxyalizarin or trioxanthraquinone discovered, and is isomeric with isopurpurin and flavopurpurin. Purpurin is not a product of the alizarin melt, but is obtained by oxidation of alizarin. Purpurin forms red needles, which begin to sublimate at 150° and melt at 253°. In boiling water, in alcohol, and other solvents it dissolves with an intensely yellow to reddish-yellow colour. Purpurin dissolves in caustic alkalies, ammonia, and carbonate

of soda, with a purple colour, redder than alizarin, flavo- and isopurpurin. The alkaline solution of purpurin, when exposed to light and air for some time, is decolorised, the colouring matter being destroyed. Purpurin dissolves in sulphuric acid with a pink-red colour; water precipitates it again. The most characteristic property of purpurin is that it dissolves in a boiling solution of alum with a yellowish-red colour and green fluorescence; the purpurin-aluminium lake also has this property. Purpurin dyes a fiery red on aluminium mordant, which, however, is less permanent and more expensive than those obtained with the two isomeric purpurins.

The distinguishing reactions of alizarin and the three purpurins are as follows:—

Name of dyestuff.	Solution in caustic soda.	Solution in sulphuric acid.	Point of sublimation.
Alizarin, . . .	Blue-violet.	Brownish-red.	Much below 160° C.
Isopurpurin, .	Violet.	Brown.	at 160°
Flavopurpurin,	Purplish-red.	Red-violet.	at 170°
Purpurin, . . .	Red.	Cherry-red.	at about 150°

In an alkaline solution of red prussiate fibres dyed with lakes of alizarin or flavopurpurin or with the aluminium lake of isopurpurin are not changed, while the iron lake of isopurpurin and the lakes of purpurin are destroyed.

COMMERCIAL ALIZARIN.

Alizarin is sold as a paste containing 20 per cent. of dry matter, representing nearly pure dyestuff, as a paste containing 40 per cent. of dry matter, and as a powder containing 80 per cent. and more. As to the storing of alizarin in paste form, see p. 570. Two essentially different shades of alizarin are distinguished, which are marked by the makers with different and contradicting letters, but which will be here referred to as alizarin V or blue shade and alizarin G or yellow shade (or for red).

(1) **Alizarin V** (violet) or *blue-shade alizarin* is the purest commercial alizarin; it contains small quantities of iso- and flavopurpurin in varying proportions, and in addition very small amounts of anthraquinone and oxyanthraquinone; the presence of these substances are proofs of the origin of alizarin from anthraquinone, whilst the alizarin from madder contains purpurin, and hence has the fluorescence characteristic of that substance.

Alizarin V forms an ochre-yellow paste (or powder). For the production of alizarin-pink the employment of alizarin V is necessary to obtain a clear and delicate tint; a pure alizarin-violet on an iron mordant can also be produced with alizarin V only (hence the name alizarin V, *i.e.*, "for violet"); alizarin G yields on an iron mordant reddish or brownish shades.

(2) **Alizarin G** (*i.e.*, "Gelb" = yellow) or *yellow-shade alizarin* or *alizarin for red* is mainly a mixture of iso- and flavopurpurin, containing also some alizarin. The commercial product forms a brownish-yellow paste (or powder). Isopurpurin is more suitable for dyeing than flavopurpurin because it resists the action of the clearing bath better; flavopurpurin is preferable for printing, because it is more readily fixed by steaming. On the other hand, if strong clearing can be dispensed with, or if high-pressure steam is applied, either compound can be used equally well.

For the production of a fiery alizarin-red, alizarin G is used, flavopurpurin giving still more yellowish shades than isopurpurin.

The methods for distinguishing the isomeric compounds have been already stated (p. 585).

The value of the dyestuffs is best estimated by comparative dye-trials. They are frequently tested by determining the percentage of dry substance; but the latter is easily increased by adulterations. If the amount of dry substance is to be ascertained, the drying temperature should not rise above 100° C.; if it does, loss by sublimation may occur. A good product should not leave more than 1 per cent. of ash on ignition and should be completely soluble in caustic soda.

Application of Alizarin V and G.—The alizarins—*i.e.*, the colouring matter of commercial alizarin—are adjective and polygenetic dyestuffs, since they are fixed exclusively with the aid of mordants, and produce with different mordants essentially different colours. They yield shades which are distinguished by brilliancy, fulness, and fastness; and are of great importance for the dyeing of the vegetable and animal fibres.

As madder was used for centuries as a dye for cotton wherever a fast red shade was required, so alizarin is now in general use; but each year the quantity of alizarin consumed in the dyeing and printing of Turkey-reds and alizarin-reds on cotton is many times greater than the largest annual production of pure colouring matter yet obtained from madder.

Fast shades of scarlet, prune, maroon, violet and black and numerous mixtures are produced both on cotton and on linen, with the aid of the various mordants, wherever fast colours are demanded.

The consumption of alizarin in wool dyeing increases steadily the more dyers learn to appreciate its valuable tinctorial properties and the better they understand how to overcome the difficulties accompanying its application (p. 575).

Silk is not extensively dyed with alizarin for the reasons given in the beginning of this chapter.

Dyeing of Alizarin on Cotton.—Aluminium, chromium, iron and tin salts are used, in conjunction with calcium salts, for the fixation of alizarin on cotton. The most important is the aluminium-

calcium mordant, which is used in various forms; the celebrated Turkey-reds and the alizarin-reds are produced with it.

Turkey-Red (Adrianople Red; Indian Red).—The method of producing a fiery and permanent red on cotton with the aid of madder roots, fatty oils (buffalo's or sheep's milk), and aluminium salts was known in the East Indies centuries ago, from whence it spread westward through Persia, Armenia, and Syria to Turkey and Greece. Since the middle of the last century the art of dyeing this brilliant red was brought by Greek dyers to Rouen, Lyons, and Languedoc in France, where several "Turkey-red" dye-works were founded. In 1765 a pamphlet, written by Le Pileur d'Alpigny,* was published by the French Government, in which full instructions are given for producing Turkey-red. As a result of this publication the process became widely known and employed in Western Europe. The first Turkey-red dye-works in Great Britain were probably founded in Glasgow in the year 1790, in which district (Vale of Leven) the Turkey-red dyeing industry of that country is still chiefly located; on the continent Turkey-red is dyed in the largest quantities in the vicinity of Elberfeld-Barmen (Prussia). In Western Europe Turkey-red was at first exclusively dyed on cotton yarn; but in 1810 Koechlin of Mulhouse introduced it as a dye for woven fabrics.

The process as it came from the East was very lengthy, requiring as much as four weeks; but the time was much shortened prior to the discovery of alizarin, some 125 years later; and now Turkey-red can be produced from madder in three days, which is as fast to light as the colour obtained by the long process. The latter is more resistant to chlorine, and slightly clearer, probably on account of the incidental bleaching of the fibre by the sun during the prolonged and frequent exposures in the fields after the repeated oiling operations; and there are dyers in various parts of the world who still use the old method and obtain for their products correspondingly higher prices; but these form a very small part of the Turkey-red produced.

During the last two decades a revolution in Turkey-red dyeing has been caused by the substitution of alizarin for madder, and by the introduction of new methods of oiling. Dyers willingly accepted the artificial dyestuff, since it was well adapted for application by the long established dyeing processes; but weavers at first complained that the yarns were too greasy and could not be sized well. Dyers, however, soon recognised the fact that the artificial dyestuff did not require such severe clearing with soap and soda as the natural products, and that the amount of oil in the preparation of the yarns could be diminished; thus this drawback was rapidly overcome, and as early as 1873 alizarin had completely displaced madder in some of the principal dye-works of Switzerland, notwithstanding the high

* *Mémoire contenant le procédé de la teinture du coton rouge incarnat d'Adrianople sur le coton filé.*

price at which alizarin was then sold. This was principally due to the brighter shades that could be obtained and the shortening of the processes of oiling and brightening (Sansone).*

Under the name of "Steiner's process" a much shorter method of oiling the goods with very hot olive oil came into use. But olive oil has been replaced in many dye-houses altogether by new preparations of castor oil (or of olive oil), the so-called Turkey-red oils, with the aid of which products the oiling operations could be reduced in number and in time without too great a loss in fastness. Thus fine shades are obtained at relatively low prices and in a short time, which are exceedingly fast to light and soap, although inferior to the red obtained by the emulsion process. Finally, we may mention various processes of dyeing a red on cotton with the aid of alizarin and aluminium mordants without any *previous* oiling of the goods, although an oiling follows the dyeing. These shades are not considered to be Turkey-reds; they are called alizarin-reds and are inferior in fastness and in brilliancy to Turkey-red; still they belong to the fastest colours produced and are dyed in very great quantities, especially on cotton piece goods.

Turkey-red, as produced on the fibre, is a very complicated compound, the basis of which probably is the calcium-aluminium lake, $(C_{14}H_6O_4)_3Al_2, CaO, H_2O$, described by Liechti and Suida (p. 580). The following series of operations serves for the production of Turkey-red:—

- (1) *Oiling* with a fatty oil (olive oil, castor oil, or Turkey-red oil).
- (2) *Sumaching*.
- (3) *Mordanting* or *Aluming*.
- (4) *Dyeing*.
- (5) *Clearing*.

A considerable number of washings are absolutely necessary between these processes in order to obtain anything like a good red colour; but the formation of the colour itself is independent of these.

(1a) *Oiling with Olive Oil*.—Oils of vegetable origin are exclusively used, olive oil being superior to all others. (In the East Indies the crushed castor-oil seeds are used.) The best kind of olive oil for this purpose is the rancid Gallipoli oil or emulsive oil (French, *huile tour-nante*) which has become rancid by the nitrogenous and extractive matter which it contains. It contains, owing to partial decomposition, more or less free fatty acids (oleic acid and others) as also free glycerin. This oil forms a milky emulsion with sodium carbonate, which emulsion may be partly a solution, and partly a mixture of the finely-divided undecomposed oil with the soap (formed by the free acid and sodium carbonate), free acid and possibly glycerin. This emulsified oil is absorbed by the fibre with special facility. The process of oiling consists in steeping the cotton-material (yarn or piece goods) in the

* *Journ. Soc. Dyers and Col.*, 1885, p. 203.

emulsion, and subsequently exposing the fibre saturated with the oil to the action of the open air (ageing), or (in Steiner's process) to an elevated temperature in ageing-rooms. To increase the quantity of oil thus deposited and transformed in the fibre the oiling and exposing process is repeated several times.

By the exposure the oil is rendered insoluble so as to adhere permanently to the fibre. The chemical reaction effecting this change probably consists in a further decomposition of the olive oil into free acids and glycerin and in an oxidation and polymerisation of the liberated oleic acid under the influence of air, light, heat, moisture, and sodium carbonate. This has not been well established, but it is well known that oleic acid is very oxidisable and disposed to polymerise; according to Camille Koechlin, 1 part of oleic acid absorbs 300 to 400 parts (by volume) of oxygen under the influence of light. The fact that when recently-oiled goods are piled up in heaps without being aired by turning, the temperature rises considerably, and may even reach spontaneous ignition, appears to favour the view that an oxidation takes place.

From the fibre which has been thus prepared and well washed, a substance can be extracted by solvents which does not contain any glycerin, and a part of which gives a soap with barium hydroxide, while another part is neutral and cannot be saponified. These compounds are probably the products of oxidation and polymerisation of oleic acid and possibly of the other components and admixtures of olive oil. The fibres which have been deprived of these substances do not yield a serviceable red with alizarin, but a fair colour is obtained when cotton is impregnated with the extract and subsequently mordanted with alumina and dyed with alizarin.

The oil as fixed in the fibres has probably a double effect:

(i.) It combines with and helps to fix the metallic mordant, as in the case of Turkey-red with aluminium and calcium, and in the very similar case of violet with iron and calcium;

(ii.) It forms a colourless transparent varnish around the colour lake which protects the same from the influence of light, air, and chemical agencies, and, at the same time, increases the lustre and fastness of the shade. It may be assumed that in the more rapid processes of preparing the cotton sufficient time is not given for the formation of this varnish-like substance; this would account for the inferior fastness of such kinds of Turkey-red.

(1b) *Oiling with Turkey-red Oil.*—The use of an olive oil which had been treated with sulphuric acid, as is now the case in the manufacture of Turkey-red oil, was recommended as early as 1834 by Runge in his work, *Farbenchemie* (chemistry of colours). During the seventies Fritz Storck and Dr. Wuth discovered, almost at the same time, the preparation of Turkey-red oil from castor oil, and by its use greatly simplified the process of Turkey-red dyeing.

The nature of Turkey-red oil has been discussed in Part V. (p. 160), and it has been stated that it contains compounds of certain organic acids with the radical of sulphuric acid, which represent either a sulphate (ester) or a sulphonic acid of ricinoleic acid. These compounds are rapidly decomposed under the influence of ageing and steaming, the sulphuric acid being separated from the organic acids and the latter being transformed into substances similar to those produced by the preparation of cotton with emulsive oil. The advantage of the Turkey-red oil over the emulsive oil is that it can be fixed in a short time by ageing, thereby allowing the laborious and lengthy exposure to the air to be dispensed with.

The cotton which has been prepared with oil (by either method) is now treated with warm water and then with caustic soda (steeping). By this operation the fibre is purified, while the oil which has been fixed on the material is not affected.

(2) *Sumaching*.—The cotton is usually saturated with a decoction of sumach after it has been impregnated with the oil. The object of this process is to introduce tannic acid into the fibre so as to render it capable of fixing, during the subsequent "aluming" operation, a larger quantity of alumina and of ultimately acquiring a fuller colour. It is uncertain whether the tannic acid enters at all into the ultimate colour lake or whether it forms a separate lake with the alizarate of aluminium and calcium. The sumaching operation is not absolutely necessary, since there is no decrease of fastness or of brilliancy of colour and no alteration of the shade if it is dispensed with. The sumaching, however, is considered by some dyers to give the colour a greater resistance towards the action of chlorine.

(3) *Aluming*.—By the process of mordanting with aluminium salts, one of the metallic mordants which is required for the formation of the red colour lake, namely, aluminium, is incorporated with the material. It is permanently fixed by the subsequent operations of ageing, washing, and chalking, while the acid of the aluminium salt is removed. Calcium, the other metallic mordant, need not be introduced into the fibre before dyeing.

Sometimes a small amount of stannous chloride or, better, stannous acetate is added to the mordanting bath to produce a more fiery shade; but what part the tin has in the formation of the colour lake is unknown. Some add the tin salt to the dye-bath or to the second clearing bath; but nothing definite can be said as to its mode of action.

(4) *Dyeing*.—The mordanted material is dyed in a bath which has been prepared with the required amount of alizarin, and which must also contain a certain amount of lime salt to form the colour lake. If the water has great temporary hardness, it contains the required amount of lime salt in the form of calcium bicarbonate; but if it is very soft, some chalk or calcium acetate must be added. It has been shown by Liechti and Suida (see above) that alizarin and aluminium do

not combine in the absence of calcium compounds; but the addition of a calcium salt causes the rapid formation of a lake, which is probably constituted according to the formula $(C_{14}H_6O_4)_3Al_2.CaO.H_2O$. Sometimes a stannous salt is added to the dye-bath, which may have the double effect of producing an alizarin-tin lake and of reducing ferric oxide, thereby preventing the latter from forming part of the colour lake; the ferric oxide, which is easily introduced into the dye-liquor as an impurity, has a very dulling effect on alizarin-red shades.

Alizarin and calcium are taken up by the fibre from the dye-bath; but the lake is not completely formed until the temperature is raised above 70° ; if the goods have been dyed at a lower temperature, as is the case in the sulphated oil process, they possess a reddish-orange colour when they are taken from the bath, and the red is developed by steaming only, which process completes the long chain of operations required for the formation of the colour-lake, provided that in the second clearing bath no further change is effected. (See *Clearing*.)

(5) *Clearing*.—The dyed goods are treated twice with hot solutions of soap. The first soaping merely removes a great amount of impurities which become attached to the fibre during the lengthy operations of oiling, mordanting, and dyeing. The utility of the addition of stannous chloride to the second soap bath is disputed. This salt makes the soap solution more neutral, sodium chloride and a stannous soap being formed. Possibly the stannous salt exerts a reducing action on the ferric compounds which may have been taken up during the preceding process and which would dull the shade, while the stannic oxide thereby formed enters the colour lake and renders the shade brighter and more fiery. It is contended, however, that stannous chloride cannot act in this way when added to the clearing bath, as the colour lake has already been formed, and that it should therefore be added to the mordanting liquor or to the dye-bath. According to another view, which is supported by Liechti's researches, a tin oleate is produced by the action of stannous chloride in the clearing bath, and is spread as a varnish over the fibre without entering into combination with the colour lake itself. Liechti has shown that 60 per cent. of the fatty acid of the soap employed may disappear and become fixed on the fibre (*Hummel*).

TURKEY-RED DYEING PROCESSES.

I. Old Process or Emulsion Process.—The process which serves for the production of the very fastest Turkey-red on cotton-yarns is conducted in the following manner:—*

1st Operation—Boiling.—The yarns are never bleached by chemicking (or treatment with chloride of lime solution), but simply freed from the naturally adhering fatty and resinous substances by "bowking,"—i.e., boiling under pressure with alkaline liquors. The general method is to

* The description of this process is taken in the main from J. J. Hummel's work, *The Dyeing of Textile Fabrics*, p. 427.

boil the yarn for 4 to 5 hours, under a pressure of 30 lbs., in a solution of caustic soda-lye of 1° Tw. Some use silicate or carbonate of soda or work in low-pressure kiers; in these cases the boiling has to be continued for 6 to 8 hours. When the yarn has been thoroughly cleaned in this way it is washed well with water, hydro-extracted, and dried in a stove at 50° to 60°.

2nd Operation—First Green Liquor.—The yarn is passed into the so-called first green liquor, which is prepared by mixing rancid olive oil with sodium carbonate and sheep- or cow-dung. The most suitable olive oil is that which forms the most perfect and permanent emulsion

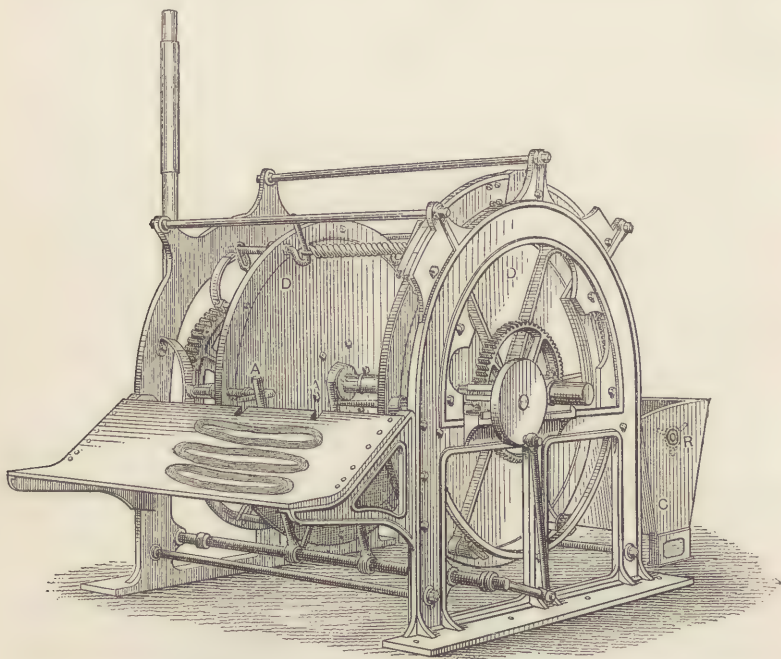


Fig. 52.—Tramping and wringing machine.

with the smallest quantity of sodium carbonate. For 100 kgs. (100 lbs.) of yarn the bath is made up with 15 kgs. (15 lbs.) of emulsive oil, 1½ to 2 kgs. (lbs.) of dung, 200 litres (20 galls.) of water, and so much of a concentrated solution of sodium carbonate as will bring the liquor to a specific gravity of 2° Tw. In this bath the yarn is thoroughly saturated with the emulsive liquor, at a temperature of about 40°, for half a minute, and then wrung out evenly. This process, usually called *tramping*, is done by "tramping machines," which steep the single hanks into the liquors and often also wring out the hanks without much hand labour. Fig. 52 shows a tramping and wringing machine by D. Stewart & Co., Glasgow, which has superseded the hand-process,

and turns off ten hanks per minute. At one end of the machine two attendants place the hanks on revolving reels, R, which run in a little cistern, C, supplied with the tramping liquor; when saturated, the hank is placed on a pair of hooks, H H₁, of which there are six such pairs carried on large discs, D, on either side of the machine. During the revolution of the discs, by a combination of rack and pinion, a twisting movement is imparted to the hank, thus wringing out the liquor, the strain being regulated by springs. Having traversed a fixed distance the hank becomes untwisted, while the pinion on the hook engages with another rack, and the hank is twisted in the opposite direction to be again untwisted and delivered from the hooks by a pair of arms, A A, fixed on a wyper shaft.

After being well prepared the hanks are thrown into heaps for the night; on the following morning they are exposed to the open air until they feel dry; and, finally, they are placed in "stoves" heated to 60° C. for 12 hours (*stoving*). In some works which produce the very best kinds of Turkey-red, as regards fastness to alkalies and to chlorine, the yarns are exposed in the open air for three or more days, and then they need not be placed in the stoves; while at the present time they are frequently brought straight into the stoves after having been piled up overnight. In this last case the steam given off in large quantities during the drying must be allowed to escape, as its retention causes the fibres to be tendered.

During the prolonged exposure of the yarns in the open air the fibre is bleached by the sun, especially in the sunny Eastern countries;* the slightly greater brilliancy of the Turkey-reds which have been produced in the East is attributable to this action.

3rd and 4th Operations—Second and Third Green Liquors.—These consist of a second and third repetition of the second operation, the object being to increase the amount of oil in the fibre. The baths are prepared exactly as for the first green liquor and the goods are steeped, exposed to the air, and stoved as before; but it is not necessary to pile them up to lie in heaps over night.

Some of the alkali which is used in preparing the bath is liberated by the chemical transformation of the oil in the fibre and dissolves, during the second and third treatment, in the green liquor which is absorbed by the yarn. The excess of this liquor which is pressed out by the wringing of the hanks, if allowed to flow back into the tramping tank, would change the specific gravity of the bath, and as it is of importance that all the liquors should be maintained regularly of the same specific gravity, only the liquor which is expressed during the steeping in the first oil bath is allowed to run back into the tramping tank; that from the second and third oil baths is collected separately and used only after being reduced to its original specific gravity by dilution with water.

* P. Lukjanoff, *Journ. Soc. Dyers and Col.*, 1886, p. 29.

About 30 per cent. of oil of the weight of the yarn is used, but only a part of this is permanently fixed in the fibre.

5th, 6th, 7th, and 8th Operations—First, Second, Third, and Fourth White Liquor Baths.—The yarn has been impregnated with oil and the latter transformed into such a state by the hanging and stoving operations that it is not readily stripped by weak alkaline liquors. A part of the absorbed oil, however, has not become insoluble or adheres superficially to the fibre. This oil is removed by repeated treatments with alkali in order to avoid the formation of "surface" colour, which is always disposed to rub and smear off.

The goods are *tramped* for this purpose four times in solutions of sodium carbonate (2° Tw.), wrung out, hung up in the open air, and "stoved" as in the previous operations; a different bath is used each time. The oil which is stripped from the fibre forms an emulsion and imparts a white colour to the baths, hence the name *white baths*. The old white baths may be used for the preparation of fresh green liquors.

9th Operation—Steeping.—The yarn is steeped for further purification in water at 55° for 24 hours, washed well and stoved at 60° . If it still contains much unmodified oil a solution of sodium carbonate at $\frac{1}{2}^{\circ}$ Tw. is used, the yarn steeped 2 hours in tepid water, washed and dried.

10th Operation—Sumaching or Galling.—An infusion is prepared of 12 kgs. (12 lbs.) of best leaf sumach for every 100 kgs. (100 lbs.) of yarn, and the cold solution is filtered and diluted to $1\frac{1}{2}^{\circ}$ Tw. The yarn, while still warm from the stoving operation, is steeped for 6 hours in the solution at 50° and then hydro-extracted. It thus takes up a certain amount of tannic acid.

11th Operation—Aluming or Mordanting.—Cake-alum is dissolved in warm water, and, when nearly cold, a cold solution of one-fourth its weight of soda crystals is added. 15 to 20 per cent. of red liquor (16° Tw.) and 0.5 to 0.7 per cent. tin crystals (of the weight of the alum) are often added to the liquor, but these additions are not essential. The addition of stannous chloride is made to prevent ferric oxide from entering into the colour lake and to introduce tin in some form into the colour, to make the shade more fiery. In this solution, which is brought to a specific gravity of 8° Tw. and kept at a temperature of 40° to 50° , the yarn is steeped for 24 hours, then thoroughly washed and hydro-extracted. By this operation aluminium salts are formed with the previously fixed oxyfatty acids and tannic acid.

The yarn, which is at last ready for dyeing, should now possess a deep yellowish tinge.

12th Operation—Dyeing.—The goods are best dyed in wooden vats with closed steam coils of tinned copper. Iron vessels must be covered from time to time with a coating of insoluble iron tannate, by boiling out with a weak decoction of sumach; if this is not done the red shade will be rendered dull by iron compounds.

The water used for dyeing should indicate 2° to 3° of hardness (Clark's scale); if it contains little or no lime, a suitable amount of ground and washed chalk (about $\frac{1}{2}$ per cent. of the weight of the 20 per cent. alizarin-paste employed) must be added. Very hard water, or water which contains iron, cannot be used in Turkey-red dyeing.

The dye-bath is prepared with 8 to 10 per cent. of alizarin (20 per cent.), 1 per cent. of tannic acid (or 3 to 5 per cent. of good sumach), and about 30 per cent. of ox-blood (of the weight of the cotton). The

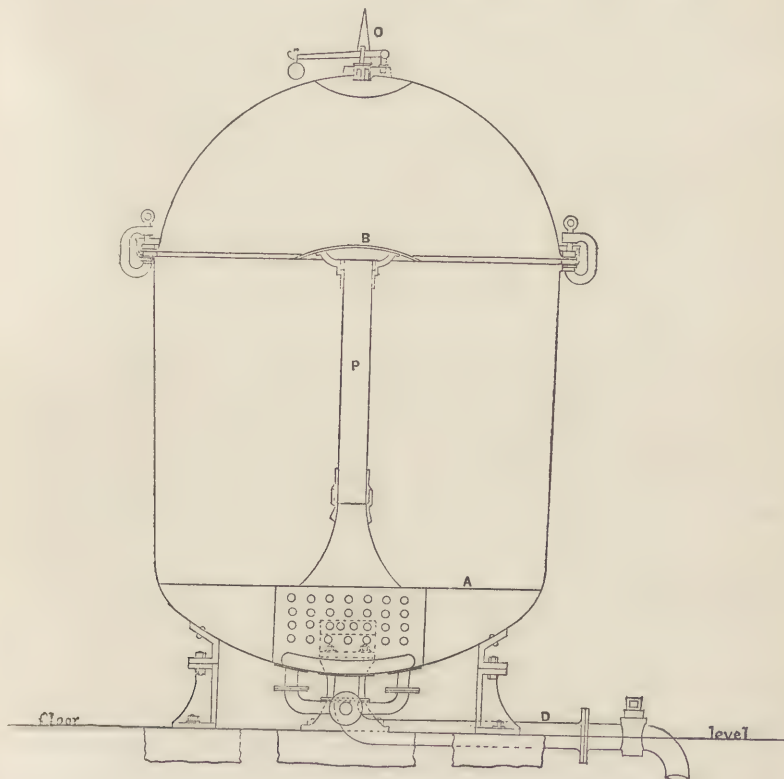


Fig. 53.

yarn is entered into the cold dye-bath, the temperature gradually raised to boiling during one hour, and maintained so for 30 to 60 minutes longer. After dyeing, rinsing in water is advisable.

The goods now possess a dull red colour, which is transformed by the "clearing" processes into the brilliant Turkey-red shade.

13th Operation—First Clearing.—The yarn is boiled for 4 hours under a pressure of 3 to 4 lbs. with about 3 per cent. of soda crystals and 3 per cent. of palm-oil-soap, dissolved in a sufficient quantity of water. The clearing boiler of D. Stewart & Co., Glasgow, is shown

in section and plan by Figs. 53 and 54. The boiler is made of copper, and the fittings either of copper or brass. The drawings show the false bottom (A), on which is fitted the (vertical) puffer-pipe (P) with the distributing cap (B) on top; under the false bottom a section of the

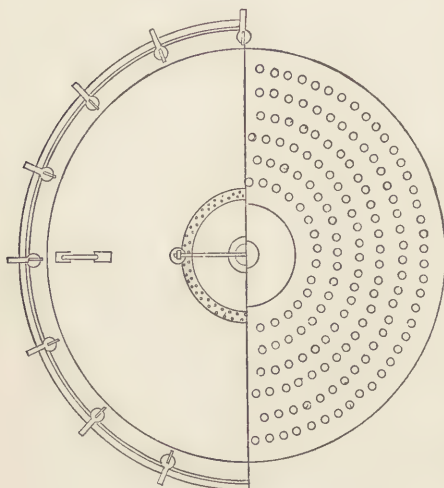


Fig. 54.

steam-coil is visible, and on the floor level the draw-off pipe (D); on top of the boiler is fitted a blow-off with safety-valve (O). The principle of working resembles that of a bleaching kier. Arrangements are fitted to keep the liquor constantly passing through the goods, which rest on a perforated false bottom, shown in plan. The liquor is boiled by a steam-coil, and forced by the steam to the top of the puffer-pipe, so as to be spread over the goods by the distributing cap;

this action is of an intermittent character, since after each boiling-over the steam under the false bottom must accumulate, until it is again able to overcome the weight of the column of water. The liquor, which is ejected through the puffer-pipe, circulates through the goods, and collects again under the false bottom.

14th Operation—Second Clearing.—The yarn is boiled for 1 to 2 hours at 3 to 4 lbs. pressure, with a solution of $2\frac{1}{2}$ per cent. of palm-oil-soap and 0.15 per cent. of tin crystals (of the weight of the cotton), and afterwards thoroughly washed in water. The excess of water is removed by mechanical means (hydraulic press or hydro-extractor), and then the goods are dried in an open-air shed. This closes the long chain of operations.

The old emulsion process of Turkey-red dyeing as now applied to yarn having been described, the simpler, less laborious, and more expeditious processes, by which very fast reds are produced, will next be noticed.

II. Steiner's Process for Turkey-Red on Cotton Piece Goods.

—In Steiner's (of Manchester) process, the repeated green liquor baths and following laborious exposures of the hanks in the open air are replaced by one padding operation in hot clear olive oil, and subsequent treatment in various soda baths and stoving. The economy in time thus effected is considerable, and the colour becomes very fast and

beautiful; indeed, of a greater brilliancy and intensity than can be obtained by the emulsion processes. The process is not used for the

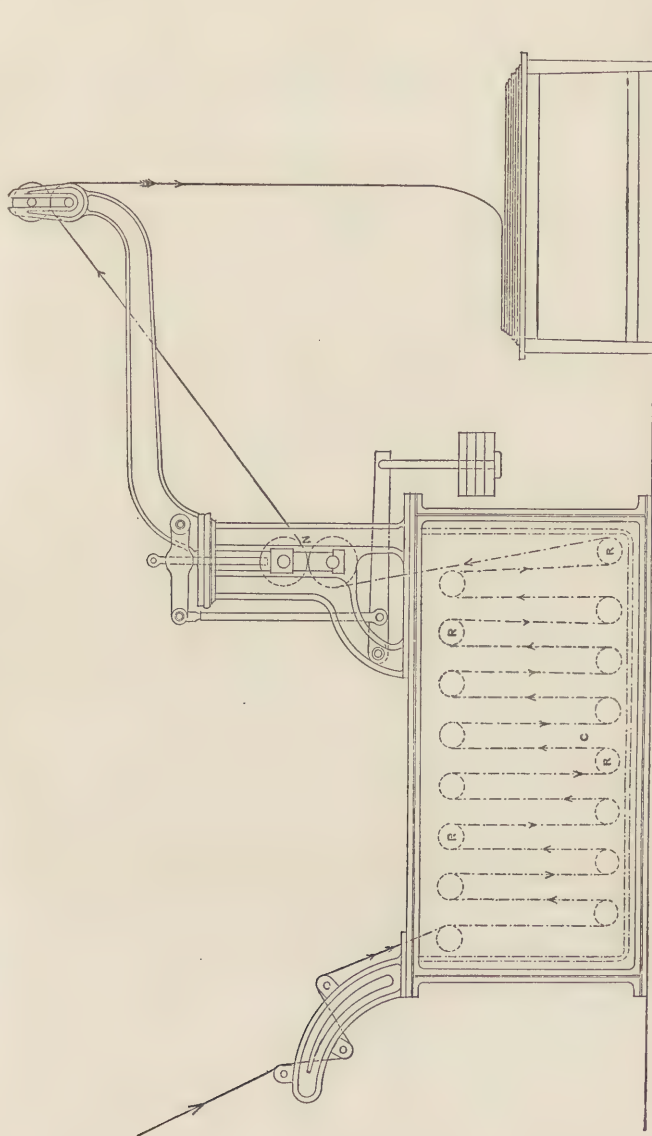


Fig. 55.—Oil-padding machine.

dyeing of yarns, on account of the difficulty of handling the yarn properly in the hot oil.

1st Operation—Bleaching.—The goods are well washed and boiled for 2 to 3 hours with water only, then boiled for 10 to 12 hours in a

solution of caustic soda, containing 2 kgs. (lbs.) of caustic soda for 100 kgs. (lbs.) cotton, and washed; finally, boiled a second time for 10 hours with caustic soda, 1.5 kgs. (or lbs.) for 100 kgs. (or lbs.) of cloth, and washed. They are then steeped for 2 hours in a solution of sulphuric acid (2° Tw.) (*souring*), washed, padded in a weak solution of sodium carbonate (4° Tw.)—to remove the least traces of free acid—and dried.

2nd Operation—Oiling.—The pieces are padded in open width in a clear solution of olive oil at a constant temperature of 110° C., and dried in the drying chamber, the temperature of which is brought as rapidly as possible up to 70°, and kept so for 2 hours. In this process no emulsive oil is employed. The oiling is done with specially-constructed machines. Fig. 55 shows an oil-padding machine of D. Stewart & Co., Glasgow. The machine consists of a steam-jacketted cistern (C) for containing the oil, and maintaining it at a certain consistency and temperature. The outside is formed of cast-iron plates, and the inside of copper plates fixed at a distance from the cast-iron, thus allowing a space for steam. Mounted inside the cistern are copper rollers (R), which guide the fabric during the immersion in the oil, after which they pass between a pair of heavy nipping rollers (N), and are loosely folded down. The cloth is passed through the oil, as indicated in the figure; before it enters the cistern, it is well opened out, and made free from creases by three stretching-bars or “openers.”

3rd to 9th Operations—Liquoring.—The oil which has been absorbed by the fibre during the hot oiling is fixed in the next operations by saponification; for this purpose, the material is impregnated with soda and hung up in heated rooms; a similar product of oxidation and polymerisation probably results thereby as in the old emulsion process.

These “liquoring” operations are totally different from those taking place in the “white baths” of the emulsion process, the latter being chiefly used for purifying purposes.

Fig. 56 shows a liquor-padding machine of D. Stewart & Co., Glasgow, which is constructed for the “liquoring” operations, and can be used for similar purposes. The liquor through which the goods are to pass is contained in a cistern (C) mounted with a number of rollers which guide the fabric during the immersion. Over this cistern two pairs of heavy nipping rollers (N, N¹) are carried by suitable cheeks, and pressure is applied by a system of levers and weights. The nipping rollers are made of various materials, such as cast iron, brass, or block tin, according to requirements. The cloth enters on the right side of the drawing, is well opened out, passed over part of the rollers, squeezed by the nipping rollers, passed over the other rollers, squeezed again by the second pair of nipping rollers, and folded down.

The pieces are padded seven times in the open width in a solution of sodium carbonate (4° Tw.), and hung, after each padding operation,

for two hours in a stove at 75° to 77° . In winter time the padding liquors are heated to 35° or 40° ; in summer time the ordinary temperature is sufficient; if the liquors become too hot, too much oil is stripped from the fibre. The padding liquors become in course of time veritable oil emulsions and their specific gravity must be maintained regularly with great care in order to obtain an even and satisfactory shade.

The quantity of oil which is permanently fixed in the fibre depends on the number of "liquoring" operations; hence their number varies with the depth of the ultimate shade which it is desired to produce.

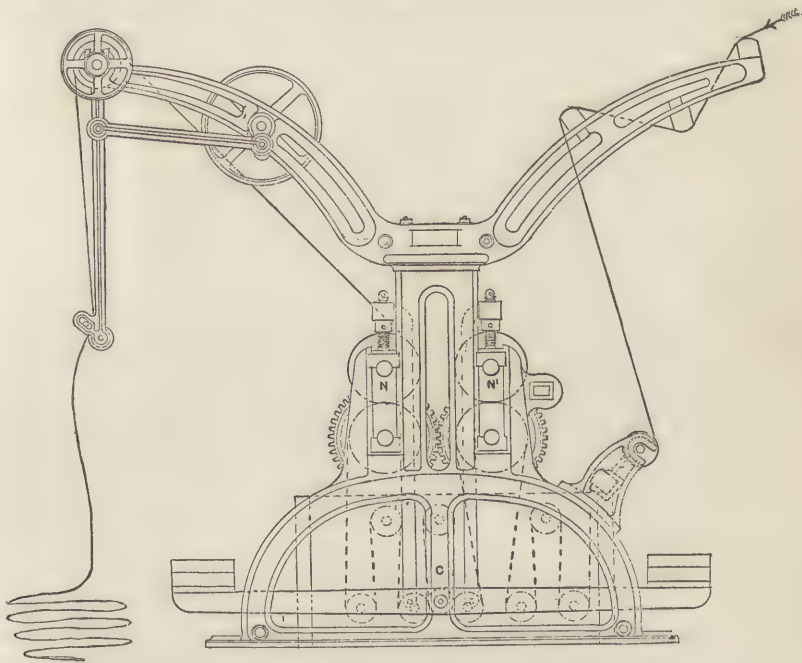


Fig. 56.—Liquor-padding machine.

Good Turkey-red which has been prepared by Steiner's process contains about 10 per cent. of modified oil in the fibre.

The drying rooms must be very well ventilated in order that the moisture which is given off may rapidly escape; otherwise the fibre is liable to be weakened.

10th Operation—Steeping.—The object of this operation is the same as that of the steeping in the emulsion process, viz., to free the fibre from all adhering oil which has not been fixed thoroughly. For this purpose the pieces are run through a vat which is divided into several compartments, fitted with rollers above and below. The first compartments are filled with sodium carbonate ($\frac{1}{2}$ Tw.) at 40° , the last with water only; after being well washed the pieces are dried.

11th to 14th Operations—Mordanting, Dyeing, and Clearing.—These operations are exactly the same as those in the emulsion process.

The chemical reactions in Steiner's process cannot be explained more exactly than those in the old emulsion process. Both are very similar and differ chiefly in the methods used for oiling the goods and for fixing the absorbed oil. They probably result in the production of the same or very similar compounds.

III. New Turkey-Red Process (for Yarn and Piece Goods)
(“*Sulphated Oil*” or “*Turkey-Red Oil*” Process).—This process has the great advantage over the old olive oil method that it can be completed in a much shorter time and with less labour; it yields beautiful red shades, which are, however, not quite as fast as the genuine old Turkey-red.

Other alizarin-colours, especially alizarin-orange, alizarin-maroon, coerulein, anthracene-brown and alizarin-yellow A and C (B.A.S.F.) and alizarin-bordeaux (Bayer) are applied by the same method.

Turkey-red oil prepared from castor oil is most generally used; sulphated olive oil can be employed, but has not proved so good, as it does not oxidise and polymerise as readily. Very good results are obtained with a carefully made castor oil soap—*i.e.*, sodium ricinoleate, but this is not used on the large scale.

1st Operation—Boiling.—This is done exactly in the same way as in the old emulsion or in Steiner's process. Bleaching has to be resorted to in the case of light shades (especially pinks) to obtain bright tints, but the action of the chlorine has to be restricted as far as possible to the destruction of the natural colouring matters of the cotton fibre, while the formation of oxycellulose must be prevented; for this reason eau de Javelle or Labarracque (chloride of potash or soda) is preferable to bleaching-powder.

2nd Operation—Oil preparing.—The washed goods are hydro-extracted, but not dried, and then worked in a bath containing 10 to 20 kgs. (lbs.) of neutralised Turkey-red oil (50 per cent.) for every 100 litres (10 galls.) of water. When thoroughly saturated with the liquor they are evenly wrung out.

3rd Operation—Stoving.—The oiled goods are dried at temperatures ranging from 40° to 60°. For the production of a bright and intense red the operations of oiling and drying and subsequent aluming are repeated once or twice. Frequently the oiled goods are steamed under a pressure of 8 lbs. for 60 to 90 minutes, but this is not essential.

The compounds constituting the Turkey-red oil are decomposed by the operations of oiling, drying, and steaming, ammonium or sodium sulphate and various organic acids being formed. The latter are similar to the corresponding substances deposited in the fibre in the older processes, and consist of products of the oxidation and polymerisation of ricinoleic acid, &c.

4th Operation—Aluming.—The goods are worked for 5 or 6 hours in

a warm bath (40° to 45°) of red liquor (10° Tw.), or of basic aluminium sulphate (10° Tw.), well wrung out and dried at 40° to 50°.

5th Operation—Chalking.—This resembles the treatments in the two other Turkey-red processes by which the material is worked in a weak alkaline bath for the purpose of purifying it from an excess of oil; in this process, however, the purification takes place after the aluming, so that not only is there a removal of oil, but also a more complete precipitation of the alumina which has been absorbed by the fibre during the aluming. A chalk bath is generally employed for this purpose (*chalking*). Brighter colours are said to be produced when phosphate of soda or ammonium carbonate are employed as fixing agents.* Arsenate of soda gives still brighter colours than the phosphate. The cotton is worked for 30 minutes at 30° to 40° in a bath containing $\frac{1}{2}$ kg. (lb.) of ground chalk per 100 litres (10 galls.) of water, then thoroughly washed and dyed without drying.

6th Operation—Dyeing.—Moderately hard water, free from iron, exactly as in the emulsion process, is required. For very deep shades about 15 per cent. of alizarin (yellow shade) is necessary; a fine pink is obtained by this process with 1 to 2 per cent. of alizarin V (purest quality of alizarin blue shade). The whole quantity of the dyestuff is added to the dye-bath, and the goods are introduced at a temperature not exceeding 25° and turned for 20 minutes; in about half an hour the bath is heated to 60° or 70° and maintained at this temperature for 1 hour (see also p. 603). After dyeing, the goods are wrung and dried with or without previous washing.

7th Operation—Second Oil-preparing.—The material is impregnated once more with a solution of neutralised Turkey-red oil (5 to 10 kgs. or lbs. per 100 litres or 10 galls.) and dried. The second oiling may be dispensed with or take place after the mordanting. In the latter case a fresh treatment in a weak solution of basic aluminium sulphate or red liquor follows for the purpose of fixing the oil.

8th Operation—Steaming.—The goods are steamed for one hour at 15 lbs. pressure or two hours without pressure to develop the colour. According to a more recent process neither oiling nor steaming follows the dyeing; the dyed goods are simply heated for some hours in water under considerable pressure. It is said that the beauty increases up to a pressure of about 65 lbs. When the goods come from the dye-bath they possess an orange tinge and a part of the dyestuff can be stripped by rinsing in water, since it is not intimately combined with the mordants. The complex lake is formed by steaming only, and the material then receives a dull red colour which is brightened by the clearing baths. Fig. 57 shows a steaming box which may be used both for yarns and for piece goods. It consists of a horizontal cylinder, one end of which is closed by a sliding door balanced by counterweights.

* J. Wolf, *Journ. Soc. Dyers and Col.*, 1885, p. 207; Kutschera and Utz, *Journ. Soc. Chem. Ind.*, 1886, p. 531.

A part of the shell is left out in the drawing so as to show the inside arrangements. The hanks or pieces are suspended on a movable framework on rails provided with bevelled wheels, which can be turned from the outside ; turning is of advantage in order to ensure regularity in

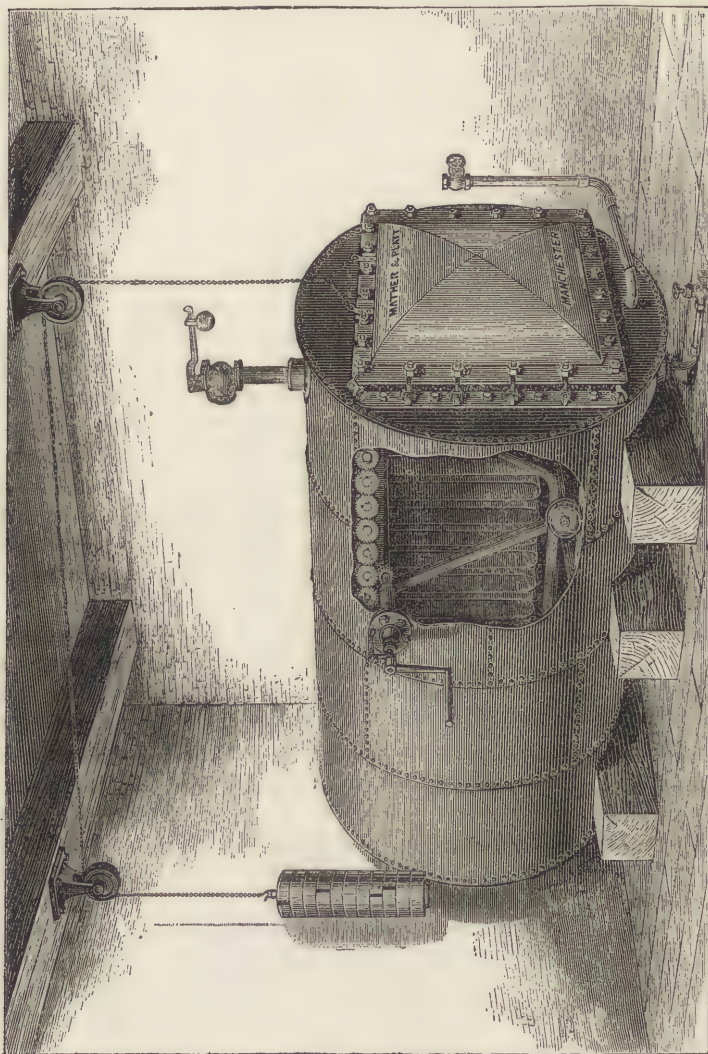


Fig. 57.—Steaming box.

the steaming and to prevent rail marks ; this arrangement, however, is not found in all steaming boxes.

9th and 10th Operations—First and Second Clearings.—These operations may be executed as in the older processes ; but less severe treatments are sufficient. A fine brilliant red is produced by once or twice boiling under 4 to 8 lbs. pressure for 30 to 60 minutes in $\frac{1}{2}$ per

cent. soap solutions (without any further additions). The soaped goods are well washed in water and dried at a moderate temperature.

The process can be simplified by raising the temperature of the dye-bath to the boiling point. In this case the oiling after dyeing is to be omitted and the steaming may be dispensed with. But the shade is never so bright or fast as that of the colours which have been produced at a lower temperature with subsequent steaming.

The simpler process, however, is well adapted for the other alizarin-colours,—e.g., alizarin-orange—since these require no steaming and a light soaping only. These are dyed with advantage in this manner.

ALIZARIN-RED DYEING PROCESSES.

By the following methods aluminium-calcium alizarin lakes are also formed and fatty acids are introduced into the lakes in some way. But the methods of dyeing and the resulting colours are essentially different from those of Turkey-red processes: (1) inasmuch as the oil is not fixed on the fibre before the mordanting and dyeing, and (2) for the fact that the ultimate colours are inferior in brilliancy and in fastness to air and light, to soap and chlorine. The inferiority of the alizarin-reds is undoubtedly due to the quantities of oil that are applied being much smaller and to the time for their transformation being shorter than in the Turkey-red processes. But it cannot be said whether the ultimate cause is a different chemical constitution of the colour lake or the absence of the supposed oil-varnish around the colour.

I. Alizarin-Red or New Red Process, with Aluminium Acetate.—The process resembles the old "madder-dyeing;" but it is much simpler, since the artificial dyestuff is much easier to dye with than the natural product. The goods are bowked and bleached with chloride of lime and then directly mordanted in commercial red liquor (aluminium acetate) 5° to 8° Tw. The goods may also be padded once or twice on the padding or printing machine; but in this case stronger liquor with some thickening is required—e.g., 5 litres (5 galls.) of red liquor (22° Tw.), 3 litres (3 galls.) of gum tragacanth water (75 grms. of gum per litre or 12 oz. per gall.), and 6 litres (6 galls.) of water.

The material, mordanted either way, is aged for 72 hours in an ageing room in which the temperature is 35° C. by the dry-, and 30° by the wet-bulb thermometer; acetic acid is driven off by the ageing, and aluminium hydroxide (or a very basic aluminium acetate) is precipitated in the fibre. In order to fix the mordant better, the goods are worked for 5 minutes at 60° in a bath, made up with a solution of phosphate, arsenate, or silicate of soda, to which, as a rule, some cow-dung is added. The bath may also be prepared with 5 litres ($\frac{1}{2}$ gall.) of silicate of soda (75° Tw.), 1 kg. (1 lb.) of chalk, 10 litres (1 gall.) of cow-dung, and 1,000 litres (100 galls.) of water. For piece goods a vat is used which is fitted with rollers above and below. When

coming from this bath the material is washed well in water and is then ready for dyeing. Piece goods are dyed in rope-form, run over a winch. 8 to 15 per cent. of alizarin, yellow shade, and half as much neutralised Turkey-red oil are added to the bath. (The usefulness of the oil in the dye-bath is disputed, and it is claimed by some that it causes a loss of alizarin.) One-half per cent. of tannic acid of the weight of the alizarin is added with advantage to the dye-bath. As to the quality of the water and the addition of chalk or calcium acetate we refer to the remarks on Turkey-red dyeing. The dyeing is started cold and the temperature raised during 2 hours to 60° or 70°, but not higher. After dyeing, the cotton is washed, dried, and impregnated with a solution of 1 litre (1 gall.) of Turkey-red oil in 10 litres (10 galls.) of water and dried in the drying-room. Finally, the goods are steamed for 1 hour under considerable pressure (20 lbs., or for a longer time at a lower pressure), soaped in $\frac{1}{2}$ per cent. soap solution at 75° for 1 hour, rinsed in water, and dried in the drying-room. Some dyers, however, soap a second time at the boil.

II. Schlieper's Alizarin-Red Process, with Aluminate of Soda (*continuous process for Alizarin-Red on Piece Goods*).—The goods are bowked and bleached as usual with chloride of lime, and then impregnated with a solution of aluminat of soda prepared in the following manner:—*Alkaline alumina mordant*: 100 kgs. (100 lbs.) of gelatinous alumina (commercial) are dissolved in 160 litres (16 galls.) of caustic soda (62° Tw.), and diluted with water to make 750 litres (75 galls.); 20 litres (2 galls.) of hydrochloric acid (31° Tw.) are added; the whole is then made up to 1,550 litres (155 galls.) and allowed to settle. For padding, this solution is diluted with $\frac{1}{4}$ of its volume of water. Some dyers add to it besides a small quantity of sodium stannite (solution of stannous oxide in caustic soda). After padding the pieces are dried on cylinders, when they assume a yellow colour; they are then aged for 12 to 24 hours in ageing rooms until the original colour is restored. The goods are then passed through a vat, with rollers above and below; first, through cold water, or through a solution of ammonium chloride or silicate of soda, and then through a tepid chalk bath. A thorough washing follows. The dyeing takes place on a jigger, through which the pieces pass slowly in open width, during 3 to 4 minutes at 90° to 95°. The bath contains per litre (per 100 galls.) $\frac{3}{4}$ grms. (12 oz.) of alizarin, and 6 grms. (6 lbs.) of clear lime water. After this follows a padding in Turkey-red oil (5 to 10 parts in 100), or, better, in a specially-prepared soap emulsion; then a steaming for 1 hour, under 15 lbs. pressure; and, finally, soaping as usual, washing, and drying.

The soap is prepared by saponification of castor oil with caustic soda-lye, and subsequent addition of sufficient hydrochloric acid to neutralise one-half of the soda; an emulsion of this acid soap in water is used.

III. Alizarin-Red, Erban and Specht's Method.—Recently a new process has been patented in Germany by Erban and Specht,* which differs totally from all previously described alizarin-red and Turkey-red processes. The patentees claim that they are able to produce red and various other shades on cotton cloth by their method.

The fibre is first impregnated with a solution of alizarin in an alkali, and afterwards with the corresponding mordant; by steaming, the colour lake is developed. The patentees proceed as follows:—Alizarin is dissolved in ammonia, and in the more or less diluted solution the tissue is padded (for dark shades twice) and then dried; the ammonia evaporates, and the colouring matter remains in an undissolved state in the fibre. Besides the alkaline solution of alizarin, the bath may receive additions that will not precipitate the colouring matter; for instance, aluminate of soda, soap, stannate of soda, or Turkey-red oil; for light shades a second bath (mordanting bath) may be thus avoided. The dried tissue is brought into the second bath (which contains the metallic mordants, the best being those which are salts of a volatile acid, as, for example, the acetates), and is dried again. By this process the formation of the colour lake is initiated. Steaming for 1 to 2 hours under 20 to 30 lbs. pressure, and clearing follow; before steaming, it is advisable to oil the goods with Turkey-red oil or soap. The same method is recommended for the dyeing and printing of alizarin and similar dyestuffs with various mordants, such as the acetates of aluminium, calcium, chromium, and iron.

Alizarin-Pinks.—Pink shades are dyed with alizarin on cotton by the methods already described; the Turkey-red oil and the various alizarin-red processes are employed, but a smaller amount of colour lake is produced in the fibre. The aluminium mordant, therefore, is applied in a more diluted form; and basic salts are avoided, because they give rise to uneven dyeing, owing to the fibre taking them up too rapidly. Neutral aluminium acetate and even normal aluminium sulphate at about 10° Tw. are used, while the quantity of oil for preparing before or after dyeing is correspondingly diminished. The dyeing is effected with 1 to 2 per cent. of purest alizarin, blue shade (for instance alizarin V 1 new, B. A. S. F.).

Owing to the difficulty of obtaining a perfectly level pink with alizarin on cotton piece goods, it is a common practice to pad the pieces with an alizarin-pink printing colour, dry, and develop by steaming.

Alizarin on Chromium Mordants.—Claret-red and maroon shades are produced with alizarin on chromium mordants, which are very fast to light, soap, and chlorine, but not equal in this respect to the aluminium and iron shades.

The general methods for mordanting and dyeing are indicated in the introduction to this chapter (p. 571). In using chromium mordant

* Germ. Pat. 54,047, *Journ. Soc. Dyers and Col.*, 1890, p. 182.

G A I (M.L.B.) for dyeing with alizarin, the commercial article should be diluted with twice its volume of water only. Redder shades than those produced with chromium mordants alone can be obtained by a combination of chromium and aluminium.

The dye-bath is prepared with the dyestuff—for deep shades about 8 per cent. alizarin—and with some calcium acetate—about one-fourth to one-fifth of the weight of the alizarin paste. If very hard water (30° or more on Clark's scale) be used the addition of the calcium salt may be dispensed with. The goods are introduced into the cold dye-bath, which is heated in the space of one hour to boiling and maintained at this temperature for two hours longer. They are then well rinsed in water, and finally soaped at 60° or at the boil, washed and dried.

Alizarin, blue shade, and alizarin, yellow shade, can be dyed on chromium mordants; the former gives bluer and more brilliant tints.

Alizarin on Iron Mordants.—Alizarin dyeing in association with iron mordants has been practised for many years. Violet shades equalling in fastness the best Turkey-reds are obtained by the Turkey-red methods by substituting a ferrous salt for the aluminium compounds and fixing it as a ferric compound in the fibre. Good lilac, purple, and dark violet shades are produced in this way. They can be obtained, however, of very satisfactory quality by less expensive methods, as there is a less demand for extremely fast colours in these tints than for fast Turkey-reds. Hence the material is not oiled (or but slightly oiled) before mordanting, and the process is chiefly used for the dyeing of cotton piece goods or for calico-printing. Alizarin, blue shade, is required, since alizarin, yellow shade, does not give pure tints with iron mordants.

Ferric salts are not suitable for mordanting, as they give rise to rubbing if precipitated as such; permanent colours are not obtained unless the ferrous compounds are oxidised after they have been taken up by the fibre. The best iron mordant is ferrous acetate or pyrolignite of iron; it gives brighter and bluer shades than ferrous sulphate, and is more readily fixed. The latter is not a good mordant, especially on unprepared cotton, since after ageing the fibre retains only a small amount of the oxide. It can be fixed, however, much better by means of a double salt of copper arsenite and calcium arsenite, prepared by boiling 1 kg. (1 lb.) of white arsenic and 1 kg. (1 lb.) of copper sulphate in 90 litres (9 galls.) of lime water, and allowing to settle, the clear solution being added to the fixing bath or print colour (*Schuetzenberger*). Oscar Scheurer* has recently shown that the arsenic can be replaced by phosphoric acid, 2 parts of the latter being mixed with 3 parts of copper sulphate (see p. 276).

The amount of iron which is taken up by the fibre depends less on

* *Journ. Soc. Dyers and Col.*, 1887, p. 193.

the strength of the mordanting liquor than on the amount of oil that has been already fixed in the material; the oil attracts the oxide of iron with great energy, so that it is not readily stripped from the fibre, even by comparatively concentrated sulphuric or hydrochloric acid. The best and bluest shades are obtained if the iron-mordant is thoroughly saturated with alizarin, while an excess of mordant imparts an unpleasant dull-red appearance; hence only a moderate preparation with oil is required for light shades, whereas for dark violets a strong oiling is of advantage.

Very deep purplish-blacks are obtained with little or no oiling by mordanting the cotton with tannin and iron by one of the methods given in part V., pp. 179-181, and 275-277. A good dark purplish-violet is produced by impregnating the cotton with iron pyrolignite (70° Tw.), drying, ageing in the Mather and Platt apparatus, and then for two days in ageing rooms, dunging in cow-dung and arsenate or silicate of soda, washing, and dyeing.

By whatever method the material has been impregnated with an iron salt, it is always passed through some fixing bath before the dyeing begins. A chalk bath is sufficient for thoroughly oiled cotton; a "dunging" bath, however, is required if the iron is only partially or not at all fixed with the aid of oil. The dunging bath, which is prepared with cow-dung and arsenate, phosphate, or silicate of soda, is used both to fix the iron completely in an insoluble form, and to remove all that has not been well fixed in the fibre. After a thorough washing, the material is ready for dyeing.

It has been previously shown that a ferric-ferrous alizarin lake can be obtained analogous with the violet ferric-calcium alizarate and the red aluminium-calcium alizarate. This ferric-ferrous compound is probably formed if sodium arsenite is added to the dye-bath, as is frequently done in order to produce faster and brighter shades. Notwithstanding this, in dyeing with very soft water some chalk or acetate of lime ($\frac{1}{2}$ per cent. of the weight of the 20 per cent. alizarin paste) should be added to the dye-bath.

The dye-bath is made up with the required amount of dyestuff—8 per cent. of alizarin V for a full shade—and about 5 per cent. (of the weight of the material) of neutralised Turkey-red oil. For bright violets 5 to 10 per cent. of methyl-violet (of the weight of the alizarin paste) are also added to the liquor. The cotton is introduced into the cold dye-bath, and the temperature is raised during $1\frac{1}{2}$ hours to 75°. After dyeing the cotton is washed, dried, steamed under 15 lbs. pressure for 20 minutes, and soaped at 60°.

Various shades of claret-red, puce, and chocolate are obtained by mordanting the cotton with a mixture of aluminium and iron salts. Some difficulty is met with in fixing the necessary quantity of iron; to overcome this, it is recommended to impregnate the cotton with tannin before mordanting with a mixture of the aluminium and iron

salts ; sometimes it is effected by adding arsenic or arsenite of calcium and copper to the fixing (dunging) bath. The arsenic may be replaced by phosphoric acid. Oscar Scheurer (*l.c.*) has drawn attention to the fact that in red liquor some sulphuric acid is generally present, forming ferrous sulphate, which compound is, as stated above, not readily fixed. The combined mordant is aged and dunged like the iron mordant alone, and the dyeing proceeds as with the iron mordant.

Moderately fast orange shades can be obtained with alizarin on cotton mordanted with *stannic oxide*; these, however, are not produced as self-colours ; but use is made of this fact in Turkey-red dyeing to give the shade greater fire, as has been repeatedly noticed.

Dyeing of Alizarin on Linen.—Linen is dyed with alizarin by processes similar to those used for cotton. Fast Turkey-red is produced in great quantities on linen yarn woven into various materials which have to stand frequent washing.

Jute is not dyed with alizarin (as stated above), since the dyestuff and the process of dyeing are too expensive for this material.

Dyeing of Alizarin on Wool.—The use of madder has not been restricted to cotton and linen dyeing ; it has been applied from an early period to the production of fast wool colours, particularly for the dyeing of fast reds on military cloth. The French Government under Louis Philippe introduced the red trousers for the French army with a view to encouraging the madder culture. Even at the present time considerable quantities of madder are used in wool dyeing, because it is easier to obtain level shades in wool dyeing with madder than with alizarin. At the present time, however, the reason why madder is still used is chiefly due to two causes : first, to the conservatism of various Governments who, in making contracts, stipulate for the use of madder in dyeing red military and similar cloth ; and, second, to the fact that it is only recently that the methods of dyeing wool with artificial alizarin have produced satisfactory results. It may be noted as an interesting fact that the Austro-Hungarian Government is adopting the use of alizarin and allied colours for the dyeing of military cloths.*

Observations on the general methods of dyeing wool with alizarin, and especially the precautions required for the production of thoroughly satisfactory colours, are given at the beginning of this chapter (p. 572).

Dyeing with Aluminium Mordants.—Alizarin yields on wool mordanted with aluminium salts red shades which are very fast to light and most other agents, but become more bluish by milling and are always prone to rub. By the addition of tin crystals to the aluminium mordant more yellowish or scarlet shades are produced, which are still less fast to milling. The vessels employed both for mordanting and for dyeing should be made of tinned copper or wood. Care

* O. Ostersetzer, *Färbereizitung*, 1890-91, p. 311.

should be taken that there is no untinned copper in any of the baths employed, since this injuriously affects the colour.

(a) *Mordanting and Dyeing Method.*—The mordanting liquor is prepared with 6 to 10 per cent. of aluminium sulphate and 5 to 8 per cent. of tartar; the latter may be replaced, partly or completely, by oxalic acid or sulphuric acid (see p. 239); in a diluted bath the sulphuric acid acts but slowly and its quantity has to be increased. Hard water is corrected with acetic acid. For very brilliant scarlets which are not to be milled severely, 1 per cent. of tin crystals is sometimes added to the mordanting bath; in this case tartar or oxalic acid should be used, not sulphuric acid.

The well purified and thoroughly wetted wool is introduced into the mordanting bath at a low temperature, the liquor is heated for 1 hour to boiling and maintained thus for 30 to 60 minutes. After being thoroughly washed in water the wool is ready for dyeing.

About 10 per cent. of alizarin (20 per cent.) are required for a full shade. The Badische Anilin-und Soda-Fabrik recommends an addition of one-fifth part of calcium acetate, one-tenth part of neutral soap, and one-twentieth part of tannic acid (of the amount of the alizarin paste) to the dye-bath to obtain colours which are fast to milling; soap, however, should be used for goods only which are to be subjected to a strong milling, since it makes the colour disposed to rub. If sulphuric acid is employed in the mordanting bath it is advisable to add 5 per cent. of sodium acetate (of the weight of the wool) to the dye-liquor. The wool is introduced into the cold dye-bath, which is heated in 45 minutes to boiling and kept so for $1\frac{1}{2}$ hours.

(b) *Single-bath Method.*—For light shades the mordanting and dyeing operation can be combined at a considerable saving, although the dye-stuff is not so completely utilized as by separate mordanting and dyeing.

The bath is prepared with 3 per cent. of alum, 2 per cent. of oxalic acid, and the necessary amount of dyestuff. If the water is soft some calcium acetate is added. The wool is entered at 20° to 30° and worked in the bath for 20 minutes; an hour is occupied in raising the temperature to the boiling point, at which it is maintained for 1 hour more. The shade is not so full and does not possess the bloom of the red dyed by the two-bath method. It stands the action of light very well, but in milling it becomes lighter. The addition of a little stannous chloride to the bath renders the shade considerably brighter, but at the same time yellower.

Dyeing with Chromium Mordants.—By far the largest amount of alizarin used in wool dyeing is applied in conjunction with chromium mordants. The shades are exceedingly fast to light and most other agents; they resist milling very well although they are somewhat changed and are more or less affected by mineral acids. Fast claret to maroon shades are produced with alizarin on chromium mordants;

by the addition of aluminium sulphate to the mordanting bath more reddish shades are obtained. The general method is indicated in the beginning of this chapter (p. 573). Wool is usually mordanted with chromium by boiling it with 3 per cent. or 4 per cent. of bichromate of potash or soda with or without 1 per cent. of sulphuric acid. Sulphuric acid makes the shade more yellowish and fuller. The best results are obtained by mordanting with 3 to 4 per cent. of bichromate and $2\frac{1}{2}$ to 3 per cent. of tartar. About 15 per cent. of alizarin-paste (of the weight of the wool) are required for a full shade.

The addition of calcium salts to the dye-bath is not absolutely necessary, but it makes the shade bluer and fuller; about 2 to 4 per cent. of calcium acetate (of the weight of the wool) are used.

Both the "mordanting and dyeing" and the "single-bath" methods are employed; the latter gives excellent results, and shades almost as full as those obtained by the two-bath method, and equally fast to light and milling. For a full shade in a single bath 15 per cent. of alizarin and 3 per cent. of bichromate of potash or soda are used. In order to obtain through and even shades, it is necessary to work first for some time in the cold, then to raise the temperature gradually to boiling, and to keep the liquid at the boil for some time.

Dyeing with Iron Mordants.—Alizarin yields on wool that has been mordanted with ferrous sulphate and tartar good violet to slate colours, which, however, are not fast to milling, and are also too expensive, on account of the considerable quantity of tartar necessary to dye them. Good and full shades demand up to 30 per cent. of tartar. The mordanting is done in a bath with 4 to 12 per cent. of ferrous sulphate, and about double that amount of tartar; the dyeing takes place in a fresh bath with 10 per cent. of alizarin, and 5 per cent. of calcium acetate, using the same precautions as with the other mordants.

The single-bath method gives similar results.

Dyeing with Tin Mordants.—Alizarin produces with stannous chloride an orange shade on wool, which is very fast to light, but is affected by milling. The presence of calcium salts in the dye-bath is not essential; 4 to 5 per cent. of calcium acetate makes the shade orange-red, an excess of calcium salt still redder, but it causes uneven dyeing; in the absence of lime the shade is much more yellowish.

(1) *Mordanting and Dyeing Method.*—Mordant the wool with 4 per cent. of tin crystals and 2 per cent. of oxalic acid; dye with 10 per cent. of alizarin with (or without) calcium acetate, as indicated for the other mordants.

(2) *Single Bath Method.*—The shade obtained with 10 per cent. of alizarin, 4 per cent. of tin crystals, and 2 per cent. of oxalic acid in one bath is as good, if not better, than one obtained by mordanting and dyeing in separate baths. The bath is exhausted.

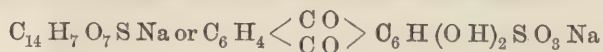
Dyeing with Copper Mordant.—Wool mordanted with copper sulphate yields a dull violet shade with alizarin; it is of no practical value. A

combination of chromium and copper mordant ($1\frac{3}{4}$ per cent. of bichrome, 1 per cent. of copper sulphate with or without $2\frac{1}{2}$ per cent. of tartar) is sometimes employed when alizarin-colours are dyed together with wood colours.

Nickel-ammonium sulphate and *uranium salts* yield useful shades of grey and slate with alizarin, on wool.

Dyeing of Alizarin on Silk.—Silk is dyed with alizarin in conjunction with aluminium, chromium, and iron mordants by the methods given on p. 575. About 20 per cent. of alizarin is required for a full shade.

ALIZARIN S (Alizarin, powder ; Alizarin-carmin).



Alizarin S is the sodium salt of alizarin monosulphonic acid ; it is obtained by the action of fuming sulphuric acid on alizarin V.

Alizarin 2 S and **Alizarin 3 S** are very similar products, which are produced by treating alizarin G with fuming sulphuric acid ; they consist of sodium monosulphonates of anthra- and flavo-purpurin, and of small quantities of alizarin S. Alizarin S is the most bluish and alizarin 3 S the most yellowish brand, while alizarin 2 S possesses an intermediate shade.

Alizarin S forms an orange powder, easily soluble in water with a yellow colour. Hydrochloric acid has no action on this solution, while caustic soda produces an intense reddish-violet colouration. Concentrated sulphuric acid dissolves the dyestuff with a brownish-yellow colour, which becomes yellow on diluting with water. Alum precipitates the dyestuff from the aqueous solution as orange flakes, which redissolve, on heating, with an orange colour. Alizarin S decomposes on being heated strongly ; splendid orange-red crystals of alizarin are obtained by sublimation.

Application.—Alizarin S is not adapted for cotton dyeing. It is used in wool dyeing only, and in large quantities, as it dyes evenly. It is especially adapted for dyeing hard spun yarns and closely woven goods, since the colouring matter penetrates the material thoroughly. For the same reason the soluble alizarin colours are employed in the Obermeier and similar dyeing machines. Alizarin S has the advantage of being a readily soluble powder, whereas the insoluble pastes are liable to dry up and to lose thereby colouring power. In dyeing, no untinned copper vessels should be used, since copper has a dulling effect on the colour ; this may, however, be remedied by adding tin crystals.

Alizarin S produces with aluminium a brighter scarlet than ordinary alizarin, with chromium a good, but somewhat light, maroon, with iron a deep violet, and with stannic oxide a fine orange-yellow. For a full shade 2 to 4 per cent. of colour are required.

Goods to be dyed with alizarin S in conjunction with alumina are

mordanted exactly as prescribed for ordinary alizarin with aluminium sulphate. The dye-bath is prepared with the required amount of alizarin S and with 500 grms. (8 oz.) of calcium acetate, 250 grms. (4 oz.) of neutral soap, and 125 grms. (2 oz.) of tannic acid for each kg. (lb.) of alizarin S employed. The goods are introduced into the cold bath, which is heated to the boil in the course of 45 minutes; after one hour boiling, 3 parts of acetic acid for each 1,000 parts of the dye-liquor are added, and the boiling is continued for half an hour. Colours are thus obtained which are very fast to light and milling. To obtain brighter colours some stannous chloride is added either to the mordanting or to the dye-bath; in the latter case, the quantity is 10 to 20 per cent. of this salt (of the weight of the alizarin S). If alizarin S is combined with ordinary alizarin, only so much acetic acid is added as is required by the former.

Alizarin S is dyed with chromium mordants exactly like ordinary alizarin, and yields extremely fast claret to maroon shades.

Iron, tin, and other mordants are of no practical importance for the application of this dyestuff.

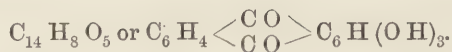
Alizarin S is especially adapted for dyeing by the "single-bath" method, owing to the solubility of the colour-lake; it is then dyed exactly as with ordinary alizarin. The colour produced in one bath, with the exception of that obtained on chromium mordants, is almost entirely removed by milling.

PURPURIN.

This dyestuff has already been described under alizarin (p. 584).

Application.—Purpurin is very little used, as it is a very expensive dyestuff, and can be replaced at a lower cost by alizarin G. It is dyed exactly as with alizarin, and yields shades similar to alizarin G. It is not so fast to light as alizarin.

ANTHRACENE-BROWN (ANTHRAGALLOL) (B. A. S. F.; M. L. B.; Bayer).



Anthracene-brown is obtained by the condensation of benzoic and gallic acids, with the aid of sulphuric acid. It is a trioxyanthraquinone isomeric with the purpurins.

Commercial anthracene-brown forms a dark brown paste (20 per cent.) which is insoluble in water, but soluble in caustic alkalies. It dissolves in ammonia with a brown, and in caustic soda with a bluish-green colour; in these solutions a brownish precipitate is produced by hydrochloric acid. Anthracene-brown dissolves in concentrated sulphuric acid with a brown-red colour; the solution gives, on diluting, a brownish flocculent precipitate.

Anthracene-brown is also sold as a dark brown powder.

Application.—Anthracene-brown is one of the fastest dyestuffs

known. It yields with chromium mordants from light drab to dark brown shades with a yellowish bloom of extraordinary fastness to light, milling, acids, alkalies, &c. It produces on aluminium a light brown, on stannous oxide a red-brown, on iron a blackish-brown, and on copper mordants a serviceable chestnut-brown shade; but the chromium colours only are of any importance.

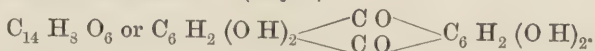
Cotton.—Anthracene-brown is used but little for cotton dyeing (except in calico-printing). It is dyed on aluminium by the simpler Turkey-red oil method given for alizarin (pp. 600 to 602), and on chromium mordants by those described in the beginning of this chapter, p. 571.

Wool.—Anthracene-brown is dyed on wool with chromium mordants by the general methods described on p. 573. 1 per cent. of dyestuff in paste-form gives a light drab, 10 to 20 per cent. a full reddish-brown shade of great fastness. The single-bath method does not give satisfactory results with anthracene-brown.

Silk.—For methods of dyeing see p. 575. 25 per cent. of anthracene-brown (paste) gives a medium brown on aluminium, a full brown on chromium mordants.

Anthracene-brown in powder is applied as follows:—The dye-stuff is dissolved in water and the colour-solution is added to the dye-bath. The wool previously mordanted with bichromate in the usual manner is introduced into the cold bath, the temperature is raised in the space of half an hour to 60°, and during the next hour a quantity of acetic acid equal in weight to the dyestuff employed is gradually added in small portions. The dyestuff is thus slowly precipitated from its solution and gradually fixed in the fibre. In the following 30 minutes the bath is brought to the boil, then 1 to 2 parts of acetic acid for each 1000 parts of dye-liquor are added, and the boiling is continued for two hours.

ALIZARIN-BORDEAUX B (Bayer).



Alizarin-bordeaux (or quinalizarin) is a tetraoxyanthraquinone which has been brought into commerce recently; it is produced by heating alizarin with fuming sulphuric acid (70 per cent. anhydride) to 170° or 180°. Commercial alizarin-bordeaux B forms a brown-red paste insoluble in water. It dissolves in caustic soda with a red-violet colour; in this solution a brown-red precipitate is formed by hydrochloric acid. Alizarin-bordeaux dissolves in concentrated sulphuric acid with a blue-violet colour; the diluted solution gives a brown-red precipitate.

Application.—Alizarin-bordeaux gives, with metallic mordants, shades which are invariably much bluer than the corresponding alizarin shades. It gives a bluish-claret shade on aluminium similar to the alizarin-chromium colour; on chromium it yields fine violet-blue

and on iron black-violet tints. Alizarin-bordeaux should be dyed without coming in contact with copper or copper salts.

Cotton.—Alizarin-bordeaux B is dyed on aluminium mordants by the new Turkey-red method (No. 3) (p. 600); on chromium mordants by the general methods given in the introduction to this chapter (p. 571). An addition of calcium or magnesium salts to the dye-bath makes the bluish shade obtained on chromium mordant redder.

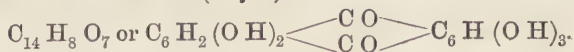
The shades are very fast to light and soap, &c.

Wool is dyed with chromium mordants and can be dyed as with the other alizarin colours. It has been observed, however, that bichromate is less suitable than chromic salts;* possibly chromic acid has a dulling effect on the colour, but wool which has been mordanted with bichromate and then passed through a solution of sodium bisulphite also gives inferior results to wool mordanted directly with a chromic salt. To obtain a good shade 4 to 6 per cent. of bichromate and 1 to 2 per cent. of oxalic acid are required. A smaller amount of chromium fluoride yields much better results, so that there is no considerable difference in cost.

The last-mentioned salt gives very good results; 2 to 4 per cent. of chromium fluoride and 2 per cent. of oxalic acid are used; the mordanting baths are preserved for further use, and are restored to their original strength by adding one-half to two-thirds of the chromium fluoride and 2 per cent. of oxalic acid. The dyeing begins at 35° to 40°, the temperature is slowly raised to boiling, and the boiling continued for 1½ to 2 hours. The colour, which shows at first a reddish shade, is by continued boiling only turned into a bluish shade and at the same time thoroughly fixed. The shade is very fast to light, milling, &c.

The *single-bath method* also gives excellent results; the shades become brighter, but less full; 4 to 6 per cent. of chromium fluoride and the required amount of dyestuff are added to the bath which is slowly heated to the boil and kept boiling for 1½ to 2 hours; chromium fluoride may be added during the dyeing without any bad effects.

ALIZARIN-CYANIN R (Bayer).†



Alizarin-cyanin R is one of the latest additions to the alizarin series; it is a pentaoxyanthraquinone and is prepared by heating alizarin-bordeaux with sulphuric acid and manganese dioxide or arsenic acid.

* *Journ. Soc. Dyers and Col.*, 1891, p. 121.

† While this book has been in the press a number of similar alizarin-cyanins have been brought into commerce by the same firm. These dyestuffs, which possess great fastness to all agents, are very valuable additions to the list of dyer's materials. The fastest of all these seems to be alizarin-cyanin-black.

The commercial product forms a dark brown paste, insoluble in water. It dissolves in caustic soda with a blue colour, and is thrown down from this solution by hydrochloric acid as a brown precipitate. Alizarin-cyanin R dissolves in concentrated sulphuric acid with a blue colour and a red fluorescence; on diluting, this solution yields a dark brown precipitate.

Application.—Alizarin-cyanin R gives very fast colours; the shades on chromium mordant resemble those obtained with alizarin-blue; the colouring power of alizarin-cyanin, however, is considerably greater. Alizarin-cyanin is sensitive to the action of metallic salts, and should be dyed in wooden tanks provided with lead pipes.

Cotton is dyed with the aid of aluminium or chromium mordants by the general methods described (see p. 571). The colour on aluminium mordant is a red-violet; while on chromium mordant a reddish-blue shade is obtained; the addition of calcium or magnesium salts to the dye-bath makes the shades fuller and more reddish. The chromium colour is very fast to soap, the aluminium colour less so; both resist light exceedingly well.

Wool.—Alizarin-cyanin R is dyed on wool exactly as with alizarin-bordeaux, and gives similar but less reddish-blue shades. The colour appears still less reddish, if the dyed wool is passed, after dyeing, through ammonia. Alizarin-cyanin R is also very fast on wool.

ALIZARIN-CYANIN G (Bayer).

This dyestuff is obtained by the action of ammonia on an intermediate product which is formed during the oxidation of alizarin-bordeaux to alizarin-cyanin R. The composition of the substance is not known.

The commercial product is a black paste insoluble in water, but soluble in caustic soda with a green-blue colour. From this solution a dark precipitate is thrown down by hydrochloric acid. In concentrated sulphuric acid alizarin-cyanin G dissolves with a red colour; the solution yields a dark precipitate on diluting with water.

Alizarin-cyanin G resembles in application and in fastness alizarin-cyanin R; but it gives much greener shades than the latter, greener, indeed, than those obtained with alizarin-green.

Anthracene-Blue (B. A. S. F.) is similar to alizarin-cyanin.

ALIZARIN-MAROON (B. A. S. F.).

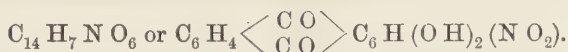
Alizarin-maroon is an amido-alizarin, the composition of which is $C_{14}H_9O_4N$, or $C_{14}H_5O_2(OH)_2NH_2$; the exact constitution and the methods of manufacture of the dyestuff are not generally known.

Alizarin-maroon is sold as a brown paste (20 per cent.), insoluble in water, but soluble in caustic soda with a violet colour; the alkaline solution gives, on diluting with water, a brown precipitate. The solution of the dyestuff in concentrated sulphuric acid is crimson-red and gives a brown precipitate when diluted. Alizarin-maroon is not

quite so fast as most of the other alizarin dyestuffs. It is dyed on cotton, wool, and silk with aluminium and chromium mordants. On aluminium it gives garnet, on chromium maroon shades.

It is dyed by the general methods used for the mordant colours (p. 570), and may be dyed with aluminium mordants like alizarin on cotton (p. 600), and on wool (p. 608).

ALIZARIN-ORANGE (NITRO-ALIZARIN).



Alizarin-orange or betanitroalizarin is formed by the action of nitrous or nitric acid on alizarin. The dyestuff is sold either as a brownish-yellow paste (with 20 per cent. of colour), insoluble in water; or as a brown-orange powder—in the form of the acid sodium salt—which dissolves in water with a claret-red colour. The powder has 4 or 5 times more tinctorial power than the paste. Both the paste and the powder dissolve in very dilute caustic soda with a crimson colour; an excess of caustic soda causes the solutions to yield a claret-red flocculent precipitate. The alkaline solutions yield orange precipitates on addition of hydrochloric acid. The solution in concentrated sulphuric acid is orange; on diluting with water a yellow precipitate is obtained. Reducing agents transform the nitro-alizarin into amido-alizarin, which dissolves in caustic soda with an intense blue colour.

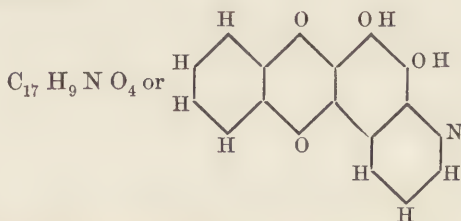
Alizarin-orange produces, with aluminium, orange; with chromium, dull brownish-red; with iron, purplish-brown; and with copper brown-red shades. Stannic oxide gives a light orange, while stannous oxide has a reducing action on the colour.

Alizarin-orange gives very fast shades. It is used on *cotton*, *wool*, and *silk* as already stated in the beginning of this chapter (see also p. 600) for the dyeing of cotton with aluminium mordants. The powder is dyed on wool with aluminium mordant like ordinary alizarin, with chromium mordant like anthracene-brown (powder) (p. 613).

Silk requires about 25 per cent. of the paste for a full shade.

Alizarin-orange is principally used for shading other alizarin-colours in wool dyeing and in calico-printing.

ALIZARIN-BLUE.



Alizarin-blue is dioxyanthraquinone-quinoline; it is produced by heating betanitroalizarin (alizarin-orange) with glycerin and sulphuric

acid to 90° when, by a complicated reaction, the new dyestuff is formed. Alizarin-blue is sold as a violet-blue paste of crystalline leaflets with a coppery lustre, insoluble in water; it dissolves in caustic soda with a green-blue colour; an excess of alkali precipitates the colour; hydrochloric acid makes the alkaline solution reddish-yellow. The solution in concentrated sulphuric acid is crimson, which colour changes to a pale orange-yellow when water is added. Alizarin-blue forms a lime-lake insoluble in water; the presence of acetic acid prevents the formation of this lake.

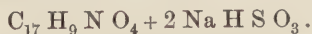
Alizarin-blue contains the two hydroxyl-groups of alizarin, and is, therefore, a weak acid; on the other hand, it is a derivative of the base "quinoline;" hence, it possesses a weak basic character, and combines with acids to form unstable salts. Alizarin-blue forms with calcium, barium, zinc, and iron, greenish-blue; with nickel and chromium, blue; with aluminium, purplish-blue; and with tin, purplish lakes. Thus, it does not show distinctly the polygenetic character of the other alizarin-colours; and also differs from them in dyeing unmordanted fibres a greenish-blue colour. Alizarin-blue in alkaline solution is reduced by zinc dust, and yields a red liquid which, when exposed to the air, resumes its original colour, forming a vat like indigo. Cotton and wool can be dyed in this vat.

Application.—Alizarin-blue has not fulfilled the expectations of those who anticipated that it would replace indigo. In vat-dyeing it cannot compete with indigo, on account of its high price and its inferior fastness to light. The colour when exposed to sunlight becomes yellowish and, after soaping, pale violet. Hence its application has been very restricted, and has only become more general since it was introduced in a soluble form (see *Alizarin-blue S*). Alizarin-blue forms insoluble lime-lakes; hence calcareous water must not be used, or, if used, must be corrected with acetic acid. Certain commercial brands possess some degree of solubility, and can be applied in the same manner as the other alizarin colours.

Cotton has been dyed with alizarin-blue by the vat-dyeing method described above; after the dyeing, the goods were passed through solutions of chloride of lime or bichromate. But this method has been abandoned, as the colours are too fugitive. After treatment with sodium bisulphite, alizarin-blue may be used in the same way as alizarin-blue S on chromium mordant.

Wool is mordanted with bichromate of potash, or with chromium fluoride, and dyed in a bath prepared with the necessary amount of dyestuff, and about double the quantity of strong sodium bisulphite. But the use of alizarin-blue S is preferable.

ALIZARIN-BLUE S (B. A. S. F.)



Alizarin-blue S is a compound of ordinary alizarin-blue with sodium

bisulphite; it is formed when alizarin-blue is mixed with a strong solution of sodium bisulphite, and allowed to stand for about two weeks.

Alizarin-blue S is found in commerce either as a dark purple powder, easily soluble in water with a brown-red colour, or as a strong solution (20 per cent.). The aqueous solution is turned blue-green by caustic soda, and reddish-yellow by hydrochloric acid. Alizarin-blue S dissolves in concentrated sulphuric acid with a brown colour; the solution becomes pale orange on diluting with water. The bisulphite compound is resolved into insoluble alizarin-blue and bisulphite, when its aqueous solution is heated to about 70°; strong acids, alkalies, or alkaline carbonates have a similar effect. Acetic or tartaric acid do not affect the compound, nor does alizarin-blue S form lakes with the acetates of calcium and chromium at the ordinary temperatures.

Application.—Alizarin-blue S has proved to be a valuable substitute for vat-indigo, in which respect it is superior to all the other artificial colouring matters known, with the possible exception of the alizarin-cyanins, which have not yet been exhaustively studied. Alizarin-blue S is very easily applied, and penetrates the fibre thoroughly; it is as fast to milling and soaping as indigo, while it has the decided advantage of not rubbing; on the other hand, it does not equal indigo in fastness to light, and does not show the fine bloom of vat-indigo shades, and is very expensive. Although alizarin-blue S is not quite so fast to light as indigo, the difference is not very great for deep shades if mordanted and dyed in the right way, without too great an excess of mordant.

Alizarin-blue S decomposes (as stated above) in solution when heated above 70°. Hence, when dissolving the dyestuff the water must not be too hot, and in dyeing the temperature must not be raised above 70° before the colouring matter has been well taken up by the fibre; if the temperature rises too high there will be unevenness and loss of dyestuff and the colour rubs. Most of the colouring matter is absorbed between 55° and 65°; on heating above 70° the bisulphite compound is decomposed, and the alizarin-blue gradually combines with the mordant in the fibre with the formation of an insoluble colour-lake.

Calcareous water is acidulated with acetic acid (about 1 part of acetic acid for 1,000 parts of soft water and more for hard water). The use of calcium salts in dyeing with alizarin-blue has no advantage, while it makes the shade decidedly duller.

Cotton.—Alizarin-blue S is dyed on cotton with chromium mordants by two methods.

(1) *Mordanting and Dyeing Method.*—The cotton is mordanted with chromium oxide, with, or without, previous oiling, and dyed as with the other mordant colours (p. 571); no calcium acetate is added to the bath).

(2) *Single-Bath or Padding Method.*—1 kg. (10 lbs.) of alizarin-blue

S (powder) is dissolved in 8 litres (8 galls.) of cold water (preferably distilled water), and when all is dissolved 1 litre (1 gall.) of chromium acetate (32° Tw.) is added. Or 3 kgs. (30 lbs.) of alizarin-blue S (paste), 6 litres (6 galls.) of cold water, and 1 litre (1 gall.) of chromium acetate (32° Tw.) are dissolved in the same manner. The cotton material is steeped in this solution; for lighter shades weaker, for darker shades stronger solutions (or repeated steeping operations) are applied. The cotton when evenly saturated with the liquor is wrung out and dried at a temperature not exceeding 40°; after drying it is steamed for 1 hour at 8 lbs. pressure, or for 2 hours without pressure; finally, it is washed, soaped, and dried. By the steaming process the bisulphite compound of alizarin-blue is decomposed and the insoluble chromium lake is formed.

Alizarin-blue S on cotton is very fast to light and exceedingly fast to all other influences.

Wool.—Alizarin-blue S is dyed on wool with chromium mordants only. For mordanting methods see p. 573; 3 per cent. of bichromate of potash gives very good results; the addition of sulphuric acid to the mordanting bath is not advisable. The chromed wool may be subsequently reduced with sodium bisulphite, or chromium salts (chromium fluoride, for instance) may be used with advantage.

The dyeing proceeds in a separate bath as usual; the single-bath method does not give satisfactory results. To obtain a good fast blue the bath must be slowly raised to boiling and maintained so until a pure shade is obtained (1 to 2 hours). Alizarin-blue S yields on wool deep indigo-blue shades, which are very fast to light and exceedingly fast to milling, scouring, and rubbing, and to dilute acids and alkalies.

Silk can be dyed with alizarin-blue S in the same way as with the other alizarin-colours with the aid of chromium mordants (p. 575). 8 per cent. of alizarin-blue S (powder) is required for a full shade.

ALIZARIN-GREEN S (B. A. S. F.)

Alizarin-green is produced by the action of very strong fuming sulphuric acid on alizarin-blue; the composition of the substance is not known.

The commercial article alizarin-green S is the bisulphite-compound and resembles alizarin-blue S. It is a dark brown liquid having a strong odour of sulphurous acid, and yields a blue precipitate on boiling (insoluble alizarin-green). The diluted aqueous solution is dark orange to reddish-brown; caustic soda makes the solution blue in the cold, but on boiling it produces a dark green precipitate; hydrochloric acid has no action in the cold, but on boiling it drives off sulphurous acid and produces a dark precipitate.

Alizarin-green, *i.e.*, the substance obtained by the decomposition of the bisulphite-compound, is dissolved by sulphuric acid with a dark blue-violet colour; on diluting, a reddish-brown precipitate is formed.

Application.—Alizarin-green S yields a dull shade of green-blue with chromium mordants, and is applied to the various fibres exactly like alizarin-blue S. Very fine effects are obtained in light shades produced with chromium mordants on cotton, especially in calico-printing.

Alizarin-green S is a very fast dyestuff.

ALIZARIN-INDIGO-BLUE S (B. A. S. F.)

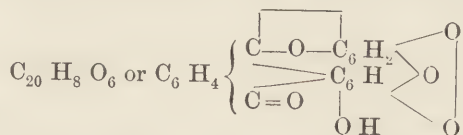
This dyestuff is obtained in the same way as alizarin-green S when alizarin-blue is heated with fuming sulphuric acid to 210° . The composition of alizarin-indigo-blue has not yet been determined. The commercial product is also a bisulphite-compound. It forms a dark red-brown liquid, which becomes brown-red to cherry-red on dilution with water. Caustic soda turns the solution blue and decomposes it on heating; hydrochloric acid has no action in the cold, but at the boiling temperature sulphurous acid is driven off and a dark blue precipitate is formed. This precipitate is dissolved by concentrated sulphuric acid with a blue colour; the solution gives a red-violet precipitate when diluted.

Application.—Alizarin-indigo-blue S gives an indigo-blue shade with chromium mordants, and is dyed on the various fibres in exactly the same way as alizarin-blue S. The shades are very fast.

COERULEÏN and COERULEÏN S.

Anthracene-green. Alizarin-green.

Coeruleïn is probably a derivative of alizarin, but has not been obtained from it yet. It is prepared by heating galleïn with twenty times its weight of concentrated sulphuric acid to 200° . The constitution is, according to Buchka, expressed by the formula :



Coeruleïn S has the composition $C_{20} H_8 O_6 + 2 Na H S O_3$.

Coeruleïn, like alizarin-blue, is sold both in the free state and under the name coeruleïn S as a bisulphite compound.

Commercial coeruleïn is a black paste (containing 20 per cent. of colour), insoluble in water. It dissolves in caustic soda with a green colour; hydrochloric acid produces in this solution a dark precipitate. Concentrated sulphuric acid dissolves coeruleïn with a dirty olive-yellow colour; the solution gives a dark green precipitate when diluted with water.

Coeruleïn yields, on being gently heated with ammonia and zinc dust, a brown-red solution, which contains coeruleïn, $C_{20} H_{12} O_6$, the leuco-compound of coeruleïn. This solution is oxidised by the air, and the original coeruleïn is reproduced. The reaction might be used for

fixing coerulein on the fibre, as is the case with vat-indigo or alizarin-blue; but the shade is without lustre. Another method of preparing a coerulein-vat for cotton (which is also applicable for alizarin-blue, gallocyanin, and similar dyestuffs) has been described in the following manner:—10 kgs. (10 lbs.) of coerulein paste are mixed in an earthenware vessel with 10 kgs. (10 lbs.) of a solution of ammonium hydrosulphite, which is prepared in the same way as the sodium hydrosulphite solution (p. 190). A "vat" is obtained by stirring well and diluting with 100 litres (10 galls.) of water; the air absorbed in the water to be used for diluting is rendered innocuous by adding $\frac{1}{2}$ litre ($\frac{1}{2}$ pint) of the hydrosulphite solution. The vat is heated with a steam-coil to 50° or 60°, and the cotton worked in it for 10 to 15 minutes, and then exposed to the air (*Bull. de Rouen*).

Another method, of great theoretical interest, has been proposed by Hunzinger. This method (which also fixes the colour without a mordant) resembles Schlieper and Baum's process of printing with indigo. Calico is prepared with glucose, and printed on with a suitably thickened mixture of coerulein and caustic soda; the material is aged in the Mather & Platt machine in order to reduce the coerulein to coerulein; the latter penetrates the fibre, and is afterwards—by ageing in the atmosphere—reconverted into coerulein.

Coerulein S is sold both as a black powder and as a black paste (20 per cent.). The powder is about four times as strong as the paste. Coerulein S dissolves in water with a dull green colour. Caustic soda produces in this solution a green flocculent precipitate which is somewhat soluble; hydrochloric acid precipitates from the aqueous solution dark flakes; on heating sulphurous acid is driven off. Concentrated sulphuric acid gives a dark brown solution, which yields a black precipitate when diluted with water.

Application.—Coerulein is used in dyeing cotton, wool, and silk, and especially in calico-printing; it chiefly serves for the production of mixed shades and mode colours. Coerulein, like alizarin-blue, is not a polygenetic colour, and gives with the various mordants similar green shades of an olive or myrtle tone.

Coerulein combines more readily with sodium bisulphite than alizarin-blue, and can be applied similarly to coerulein S if it is mixed in the dye-bath with the necessary amount of bisulphite. It is even said to give faster colours in this way.

In dyeing with coerulein, the water must be acidified with acetic acid to prevent loss by the formation of insoluble lime-lakes.

Coerulein does not combine well with alizarin-orange as the latter requires calcareous water; for the shading of coerulein anthracene-brown is better than alizarin-orange.

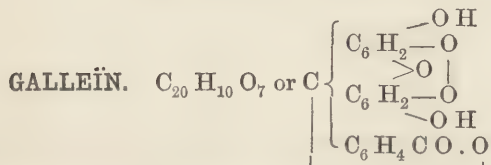
The following remarks apply only to coerulein S; but coerulein can be used in the same way after being treated for three days with one-third of its weight of bisulphite of soda.

Cotton.—Coerulein can be dyed on aluminium mordant by the new red process (p. 600); the mordanted cotton, however, should not be worked in a chalk bath before dyeing; phosphate or silicate of soda or similar fixing agents should be used. For dyeing, water free from lime must be used, and the dye-bath should have 20 cc. (1 gall.) of neutralised Turkey-red oil per litre (50 galls.) added to it. A fast medium shade of green is obtained. Iron yields a dark olive-green. The mordant almost exclusively used for the fixing of coerulein is chromium; and the dyeing is effected in the usual way (p. 571). Very fast and dull olive-green shades are obtained with chromium mordants, which equal the best alizarin colours in fastness. Other green dyes, such as chrome-green and aniline-green, are brighter, but not nearly so fast. The single-bath method is applicable. (See *Alizarin-blue S.*)

Wool.—Coerulein is dyed on wool with chromium mordants only, which give excellent results; the fullest shades are obtained if bichromate and tartar are used in mordanting, or if the wool is first mordanted with bichromate and sulphuric acid, and subsequently passed through a bisulphite solution. Coerulein is dyed by the ordinary methods (p. 573), and yields from pale sage-green to very dark green shades, which are extremely fast to light, milling, &c.

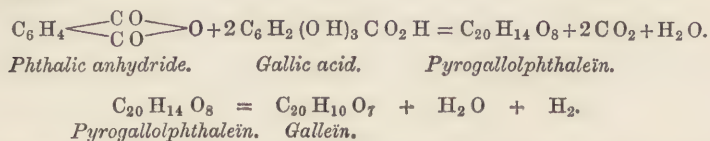
Silk (see p. 575).—About 25 per cent. of coerulein S (paste) is required for a full shade with a chromium mordant; aluminium mordants can also be employed.

DERIVATIVES OF PYROGALLOL.



Anthracene-Violet. Alizarin-Violet.

Gallein is produced by heating phthalic anhydride with gallic acid to 200°. The gallic acid is thus resolved into carbon dioxide (which escapes) and pyrogallol; the latter forms with phthalic anhydride pyrogallolphthalein, which is transformed into gallein by spontaneous oxidation:



Gallein loses one equivalent of water by the action of concentrated sulphuric acid at 200°, and is thereby transformed into coerulein.

Gallein is sold as a violet paste, containing 20 per cent. of dry

colouring matter, or as a violet powder. The pure substance, which can be obtained from the dark red alcoholic solution, forms a green crystalline powder with a green reflex. Gallein is sparingly soluble in boiling water, and forms a red solution; it dissolves in caustic soda with a violet-blue colour, which is turned orange by hydrochloric acid with formation of a dark yellow precipitate. The solution in sulphuric acid is a dark yellow, and yields on diluting a finely-divided precipitate, without changing its colour. Gallein forms with the alkalies and alkaline earths, red, violet, and blue soluble compounds; with the oxides of aluminium, chromium, and iron, red to blue-violet insoluble colour lakes. Gallein is reduced by alkaline reducing agents, and forms at first the leuco-compound *hydrogallein*, $C_{20}H_{12}O_7$, and, on further reduction, gallin, $C_{20}H_{14}O_7$.

Application.—Gallein is used for dyeing and printing the various fibres; it is always fixed with the aid of mordants, chromium mordants being almost exclusively used. It dyes evenly and combines well with the alizarins, but its high price, combined with its inferior fastness to light, prevents its extensive application as a colouring matter.

Cotton is mordanted with alumina or chromium oxide, or ferric oxide, and dyed in the way described on p. 571.

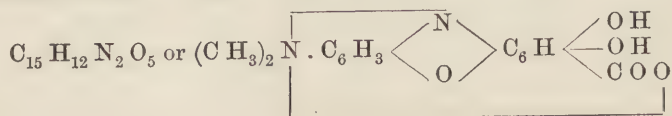
Gallein yields reddish-violet shades on aluminium and on chromium; a dark violet shade on iron mordants. The colour when dyed with chromic oxide is fairly fast to soaping, but is not much faster to light than methyl-violet.

Wool.—Gallein is dyed on wool mordanted with bichromate of potassium; an addition of sulphuric acid to the mordanting-bath and a subsequent passage through a solution of sodium bisulphite produces the fullest shades. About 10 per cent. of gallein paste are required for a full colour. The methods of dyeing are described on p. 573. Gallein powder is used in the same way as anthracene-brown powder.

Gallein dyed on chromed wool produces a full violet, which is only moderately fast to light but nearly fast to milling; the colour does not rub. When dyed on an aluminium mordant the colour is slightly redder and less fast; on tin mordant a moderately fast violet-red is produced.

Silk.—Gallein can be dyed on silk with the aid of aluminium and chromium mordants; for a full shade about 40 per cent. of paste is required. (See p. 575.)

GALLOCYANIN or FAST VIOLET D H (Durand).



Gallocyanin is produced by the action of nitrosodimethylaniline hydrochloride on gallic acid and belongs to the oxazine-compounds.

It possesses by virtue of its chemical constitution both basic and acid properties; the salts which it forms with mineral acids are red, those with metallic oxides are blue-violet. The alkaline salts are soluble; those with the alkaline earths and heavy metals are insoluble or sparingly soluble. Alkaline reducing agents convert gallocyanin into a leuco-compound, from which the original colouring matter is regenerated when exposed to atmospheric oxygen. Gallocyanin is sold as a greenish-grey paste, insoluble in water; it dissolves in caustic soda with a deep violet colour, which becomes crimson on addition of hydrochloric acid; the paste dissolves also in hydrochloric acid to some extent with a light crimson colour. The solution in sulphuric acid is blue and becomes crimson on diluting with water.

Gallocyanin B S or Fast Violet B S is the compound of gallocyanin and bisulphite. It can be prepared by mixing 1 kg. (10 lbs.) of gallocyanin with 15 to 30 cc. (1 to 2 pints) of sodium bisulphite (75° Tw.), the mixture being allowed to stand for about 24 hours. Its blue aqueous solution is used in dyeing, and can be bought ready for use, or be prepared by the consumer.

Application.—Among the many colouring matters which have been discovered during the last decade, gallocyanin is second to none in importance, owing to the beauty and relative fastness of the colour, and the diversified applications to which it is adapted. Its fine blue-violet shade is valuable as a self-colour, and in combination with the wood-colours, alizarins, and other dyestuffs which dye on chromium mordants, it is suitable for the production of an endless variety of shades.

Gallocyanin is always fixed with chromium mordants.

Cotton is mordanted with alkaline chromium mordant, or by any other of the indicated methods. The manufacturers of the article have recently recommended the following mode of procedure:—Soak the cotton for some hours in chromium chloride (32° Tw.), wring, and pass through a cold bath of sodium zincate (3° Tw.), wring again, wash, and expose to the air for some time. The chromium oxide is fixed by the action of the zincate, and a double mordant of chromium and zinc is precipitated. The zincate of sodium is prepared either by dissolving zinc or zinc oxide in caustic soda, or by adding caustic soda to the aqueous solution of a zinc salt until the precipitate at first formed is redissolved (see p. 304). The two mordanting baths are used continuously, and their strength is restored as required. The dyeing with gallocyanin is started with a fresh cold bath, which is gradually heated to the boil, and kept boiling for one hour.

Gallocyanin yields a bright blue-violet shade, which resists light, soap, and acids very well, but is not fast to soda. For a full shade 7 to 8 per cent. of gallocyanin (of a paste of 20 per cent. strength) are required. The colour can be turned to indigo-blue by adding Persian berries extract, fustic, or quercitron, or 0.1 to 0.2 per cent. of methylene-blue,

and 1 to 2 per cent. of tannin to the dye-bath; in the last case, gallo-cyanin acts as a mordant towards methylene-blue, and fixes this dye-stuff. By combination of gallo-cyanin with alizarin, coerulein, &c., a great variety of shades is produced.

The dyestuff can also be fixed with the aid of tannin and antimony in the same way as the basic colours; but this method does not offer particular advantages.

Wool is mordanted with bichromate; the best results are obtained by mordanting with bichromate and subsequently passing through sodium bisulphite; the last operation may be dispensed with if the bisulphite-compound is used for dyeing.

Enter cold, heat slowly to the boil, and boil for some time. 10 per cent. of gallo-cyanin give a full shade; the addition of calcium acetate to the dye-bath is beneficial. The pure blue-violet shade, although inferior to alizarin-blue, may be considered very fast to light and to milling. By combination with other mordant colours compound shades are easily produced.

Aluminium, iron, copper, and tin mordants produce similar shades with gallo-cyanin as chromium mordants, which, however, do not possess the same brilliancy and permanence.

GALLANILID-BLUE (Durand).

Gallanilid-blue is produced by the action of gallanilide on nitrosodimethylaniline and subsequent treatment with aniline. Its sulphonic acid has been described as gallanilic indigo P S. (See under *Acid Colours*, p. 550.)

Gallanilid-blue is similar to gallo-cyanin, and is applied in the same way. It dyes a somewhat bluer shade.

GALLANIL-VIOLET B S (Durand).

Gallanil-violet B S is the bisulphite-compound of *gallanil-violet*, which is produced by the action of gallanilide on nitrosodimethylaniline. Gallanilid-blue and gallanilic indigo P S are phenylated derivatives of gallanil-violet. It forms an olive-green paste, which is insoluble in water, and dissolves in caustic soda with an intense violet colour. Hydrochloric acid turns this solution reddish-violet and produces a reddish-violet precipitate. The solution in concentrated sulphuric acid is reddish-violet and gives a reddish-violet precipitate on diluting with water.

Application.—Same as gallo-cyanin; the shade is nearly the same.

DELPHIN-BLUE (Kern). CRUMPSALL FAST BLUE (Levinstein).

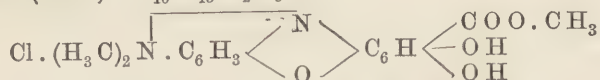
Delphin-blue is the sulphonic acid of a product obtained by heating gallo-cyanin with aniline. The commercial product is sold either as a dark paste (in the form of the free sulphonic acid) or as a dark brown powder (in the form of the ammonium salt). The latter dis-

solves in water with an intense violet colour. The dyestuff is precipitated from this solution by hydrochloric acid, while caustic soda gives a soluble reddish precipitate. The solution in sulphuric acid is red-violet and does not change in appearance on diluting.

Application.—Delphin-blue is dyed on metallic mordants, chiefly on chrome, and is specially adapted for wool dyeing. Bichromate with tartar is the best mordant; bichromate with sulphuric acid gives less bright colours. It gives greenish-blue shades on *cotton* and may be dyed on this fibre in the same way as gallocyanin. It dyes on *wool and silk* bluer shades than those obtained with gallocyanin. The single-bath method does not yield fast shades; but such are obtained by saddening with salts of copper or iron. Mordanting with bichromate, copper sulphate, and tartar or sulphuric acid produces colours which are very fast to light and milling, though not very bright. Aluminium gives redder shades, which are not very fast.

Delphin-blue or Crumpsall fast blue when dyed on unmordanted wool produces violet colours, which are not fast to soap or light.

PRUNE (Kern). $C_{16}H_{15}N_2O_5Cl =$



Prune is the methyl-ether of gallocyanin, and is produced by the reaction of nitrosodimethylaniline hydrochloride with the methyl-ether of gallic acid.

Prune forms brown glittering crystals, or a dark brown powder, and is readily soluble in water with a red-violet colour. The aqueous solution becomes crimson on addition of hydrochloric acid, and yields with caustic soda a soluble violet precipitate. The solution in sulphuric acid is blue, and becomes crimson on diluting with water.

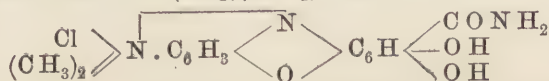
Application.—Prune is chiefly used in calico-printing and is fixed with the aid of metallic mordants; it can also be printed with tannin.

Cotton is dyed, as with the basic colours (on a mordant of tannin and antimony, p. 452), or it is mordanted with an aluminium salt and dyed in a very slightly alkaline bath with prune. Prune dyes plum shades, which are fairly fast to soap.

Prune can also be dyed in combination with dinitrosoresorcin on iron mordant and produces then a good black.

Wool can be dyed with prune by the general methods (p. 573) on chrome mordants. The colour is suitable for combinations with other mordant colours.

GALLAMINE-BLUE (Geigy). $C_{15}H_{14}N_3O_4Cl =$



Gallamine-blue is produced by a modification of the process for pre-

paring gallocyanin, gallaminic acid ($C_6H_2(OH)_3CONH_2$) being used instead of gallic acid.

The commercial product is a dirty green paste, slightly soluble in boiling water with a green colour; it dissolves more readily in hydrochloric acid with a red colour and in caustic soda with a violet colour. The solution in sulphuric acid is red and in thin layers green, and remains red on diluting with water.

The colour is also sold in the form of a bisulphite compound.

Application.—Gallamine-blue is recommended for the production of compound shades in calico-printing and wool dyeing. It produces on wool which has been mordanted with bichromate of potash and tartar a blue-violet similar to gallocyanin, which, however, is partly discharged by soap or acid, and is but moderately fast to light.

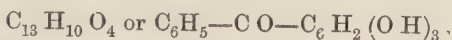
GALLOFLAVIN (B. A. S. F.) $C_{13}H_6O_9$ (?)

Galloflavin is produced by moderate oxidation of gallic acid in an alkaline solution; the constitution of the compound is not known.

The commercial article forms a dull greenish-yellow paste containing 20 per cent. of colouring matter; it is insoluble in water, but dissolves in caustic soda with an orange colour, and is precipitated from this solution by hydrochloric acid as a yellowish flocculent mass. Galloflavin dissolves in sulphuric acid with a yellow colour; the solution yields a yellowish-grey precipitate on diluting. Galloflavin when dyed on mordanted wool yields with bichromate mordant an olive-yellow, with copperas a dark brown, with stannous mordant a dull orange, and with copper sulphate a brown shade.

Application.—Galloflavin combines well with the alizarins, and is used in dyeing and printing cotton, wool, and silk; for fixation, chromium mordants only are used, and shades similar to old fustic are obtained, which are fairly fast to light, soap, and milling, but do not compare favourably with the alizarins. The colour is somewhat sensitive to chlorine. The general methods given in the introduction (pp. 570 to 576) are applicable.

ALIZARIN-YELLOW A (B. A. S. F.)

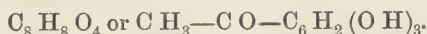


Alizarin-yellow A or *trioxybenzophenone* is (like the following alizarin-yellows) not a true alizarin colour. It is produced by condensation of benzoic acid or benzotrichloride with pyrogallol, and is sold as a grey paste, which dissolves in boiling water; hydrochloric acid has no action on the solution; caustic soda dissolves the paste, producing an intensely yellow solution which is soon changed by oxidation. The solution in sulphuric acid is yellow; on diluting, a pale yellow precipitate is obtained.

Application.—Alizarin-yellow A is used in cotton dyeing, and especially in calico-printing, on aluminium mordant. It produces

orange-yellow shades, which are fairly fast to light, soap, and chlorine. The third Turkey-red method in its simplified form (p. 600) is used for dyeing.

ALIZARIN-YELLOW C (B. A. S. F.)



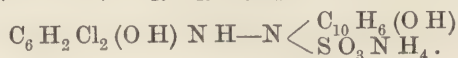
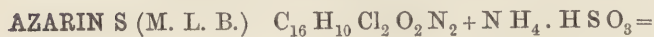
Alizarin-yellow C or *gallacetophenone* is produced by the action of glacial acetic acid and chloride of zinc on pyrogallol. Its chemical constitution is simpler than that of any other organic dyestuff, with the exception perhaps of picric acid.

The commercial article forms a grey paste containing 20 per cent. of dry colouring matter, which dissolves freely in hot, less in cold, water; hydrochloric acid has no action on the solution; caustic soda colours it brown, and changes the dyestuff by oxidation. The colouring matter dissolves in sulphuric acid with a yellow colour; the solution yields a yellowish precipitate on diluting.

Application.—Alizarin-yellow C is used, like alizarin-yellow A, chiefly for calico-printing with the aid of aluminium mordant. It yields fairly fast shades. On aluminium, greenish-yellow; on chromium, brown; on iron, slate to black colours are obtained.

For methods of dyeing, see p. 600.

VARIOUS PHENOLIC COMPOUNDS.



Azarin S is a compound of *dichlorphenolazobetanaphthol* and ammonium bisulphite. The azo-compound is not soluble in water, but it is converted by the action of ammonium bisulphite into a soluble hydrazo-compound, which is dissociated by a high temperature similarly to alizarin-blue S, &c. On this property is based its application in dyeing and printing.

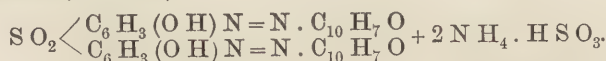
Azarin S comes into commerce as a yellow paste, very similar to alizarin in appearance, but smelling of sulphur dioxide; it dissolves sparingly in water with a yellow colour; hydrochloric acid produces in this solution an orange-yellow precipitate; caustic soda forms a violet precipitate with a red colour. Sulphuric acid dissolves the dyestuff with a crimson colour; on diluting, the solution yields a red-brown precipitate.

Application.—Azarin S is used for the preparation of beautiful red and pink lakes, which resist the light very well. It is also used for the dyeing of cotton and silk, as also in calico-printing, and is applied in the same way as alizarin-red; only, it requires in addition to the aluminium mordant, a stannous compound for fixation. The following

process is recommended for cotton piece goods:—Mordant on the padding machine in a bath containing 10 parts of aluminium acetate (12° Tw.), and 1 part of stannous hydrate paste, age* for 12 to 24 hours, dung in cow-dung or in a chalk bath at 55° , wash, and dye; prepare the dye-bath with 3 parts of azarin (20 per cent.) and 1 part Turkey-red oil, raise the temperature in one hour to 75° or 80° , dry, pass through Turkey-red oil, steam, wash, and soap.

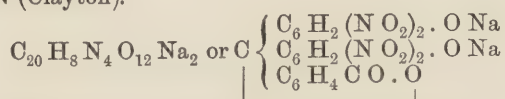
Azarin S dyes a very bright red shade, somewhat bluer than alizarin, which is very fast to soap, but inferior to alizarin in fastness to light. The high price prevents an extensive employment of the product.

AZARIN R (M. L. B.)



Azarin R is the azo-compound of diamido-oxysulphobenzide and betanaphthol, combined with ammonium bisulphite. It resembles azarin S.

AUROTIN (Clayton).



Aurotin is the sodium salt of *tetranitrophenolphthaleïn*. It forms an orange-yellow paste, which dissolves in water with an orange colour. Hydrochloric acid separates the free colour acid, which melts at 244° ; caustic soda has no action on the solution. Sulphuric acid dissolves the colouring matter with a brown-orange colour; the solution yields an orange precipitate on diluting with water. The most characteristic reaction of aurotin is that with stannite of soda in the presence of an excess of caustic soda, by which the yellow colour of the solution rapidly changes to an intense indigo-blue.

Application.—Aurotin is used in wool dyeing, and can be fixed both as a direct acid colour and as a mordant dyestuff, with the aid of chromium mordants.

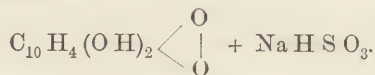
Dyeing without Mordants.—Dye in a bath which has been prepared with the required amount of colour and has been acidulated with acetic acid—sulphuric acid and bisulphate are less suitable. Enter cold, heat very gradually to the boil, and work until the bath is exhausted ($1\frac{1}{4}$ to $1\frac{1}{2}$ hours). A reddish-yellow shade is obtained similar to that of tartrazin; it is fairly fast to light and milling, and does not bleed into the white.

Dyeing Mordanted Wool.—Boil the wool for $1\frac{1}{2}$ hours with 3 per cent. of bichromate and 2 per cent. of sulphuric acid and rinse in water. Dye in a fresh neutral bath with 2 per cent. of aurotin; enter cold and heat to the boil; work until the bath is exhausted. Aurotin yields in

this way very fast colours, which somewhat resemble those obtained with old fustic.

For shading purposes the wool can also be mordanted with 2 per cent. of bichromate, 2 per cent. of copper sulphate, and 2 per cent. of sulphuric acid.

ALIZARIN-BLACK S (B. A. S. F.)



Alizarin-black S is the bisulphite-compound of *dioxynaphthoquinone* or *naphthazarin*. It is produced by the action of zinc and concentrated sulphuric acid on alphanitronaphthalene and subsequent treatment of the quinone thus obtained with sodium bisulphite. The bisulphite-compound is stable towards the action of hydrochloric acid or diluted sulphuric acid; by ammonia, caustic alkalies, and alkaline carbonates it is resolved into the two components. The same decomposition takes place in dyeing; dioxynaphthoquinone is liberated on heating, and combines with chromium hydroxide to form the colour lake.

Alizarin-black S forms a black paste smelling of sulphur dioxide, and is soluble in cold water with a red-brown colour; hydrochloric acid has no action on the solution, caustic soda turns it blue. The solution in sulphuric acid is dark olive and becomes red on heating, evolving the smell of sulphur dioxide; the olive solution yields a dark brown precipitate on diluting.

Application.—Alizarin-black S is principally used in calico-printing and in wool dyeing for the production of extremely fast slate and black shades with the aid of chromium mordants; but it is not extensively employed in cotton dyeing, since it is difficult to obtain full shades, and the colouring matter is too expensive.

Cotton is mordanted with H. Koechlin's alkaline chromium mordant (p. 256) and dyed in a concentrated bath, with the addition of acetic acid (3 parts for 1000 parts of dye-liquor) and common salt (25 per cent. of the weight of the material); 40 per cent. alizarin-black R are required for a full shade. A reddish-black is obtained which is extremely fast to all agents; a jet-black may be produced by shading with coerulein or other mordant-colours. Alizarin-black may be dyed exactly like alizarin-blue S by the single bath or padding method (p. 618).

Wool is mordanted with bichromate and dyed by the methods given on p. 573. 3 per cent. of alizarin-black S is required for a slate shade and 20 to 35 per cent. for a full black (which appears slightly reddish). The colour combines well with other mordant dyestuffs, and is exceedingly fast to light, milling, rubbing, acids, and alkalies.

Alizarin-black may be employed with advantage for the production of full shades in *one* bath, whereas the other alizarin colours do not yield very deep shades by this method. The makers of alizarin-black

recommend the following process :—Prepare the bath at a temperature not exceeding 50° C., with 6 kgs. (lbs.) chromium acetate, 32° Tw., for 100 kgs. (lbs.) of wool; enter the material and boil for one hour, cool with cold water to 70°, add the required amount of colouring gradually, and boil one hour more. After this time, add, to develop the shade completely, 3 to 4 kgs. (lbs.) liquor ammoniæ for every 100 kgs. (lbs.) of material, and boil again for half an hour; finally, rinse well.

Another process of dyeing alizarin-black by the one-bath method, which was also proposed by the makers, consists in boiling unmordanted wool with 35 per cent. of alizarin-black in a concentrated bath for one hour, adding a solution of 10 per cent. of alum, 1 per cent. of copper sulphate, and $\frac{1}{2}$ per cent. of oxalic acid to the bath and boiling $1\frac{1}{2}$ hours longer. The black will be bluer if, after this time, 1 to $1\frac{1}{2}$ parts of ammonia are added to the dye-bath for every 1000 parts of liquor, and the boiling is continued for half an hour. While adding the ammonia, the wool has to be taken out. It is doubtful, however, whether the wool is not injured by the boiling with ammonia.

Silk is dyed with the help of chromium mordants by the methods given on p. 575.

Alizarin-black can also be dyed on silk without boiled-off liquor; in this case a concentrated bath is required containing 7 parts of alizarin-black paste in 100 parts of water. Enter cold, heat gradually in the space of 45 minutes to the boil, and boil for one hour longer; wring and rinse well; soap for 15 minutes in boiling soap solution, 2 grms. per litre ($\frac{1}{3}$ oz. per gall.), brighten with acetic acid; wring and dry.

An iron mordant is also recommended by the makers for dyeing alizarin-black on silk in the following manner :—Work the silk for half an hour in nitrate of iron (52° Tw.), rinse, soap for $1\frac{1}{2}$ hours at 75° C. in a 10 per cent. solution of neutral soap, and rinse again. After this, work the silk in a bath of 10 per cent. yellow prussiate of potash and 20 per cent. hydrochloric acid (which treatment imparts a bluish tone, cf. p. 281), and steep for 2 hours at incipient boiling in a solution of 50 per cent. catechu (of the weight of the silk); rinse again. Dye with 30 per cent. alizarin-black W R in a bath containing 5 per cent. neutral soap and a small amount of acetic acid; enter cold, heat in 1 hour to the boil, and continue boiling for $1\frac{1}{2}$ hours.

AZO-COMPOUNDS.

CLOTH-RED G (Oehler). CLOTH-RED G EXTRA (Bayer).



Cloth-red G is an acid azo-dyestuff produced by the action of diazotised amidoazotoluene on betanaphthol sulphonic acid S. It forms a red-brown powder, which dissolves sparingly in water with a

brown-red colour; hydrochloric acid forms in the aqueous solution a brown-red precipitate; caustic soda produces a yellowish-brown precipitate which dissolves in pure water. Sulphuric acid dissolves the dyestuff with a blue colour; the solution yields a brown-red precipitate on diluting. Cloth-red is readily precipitated from the aqueous solution by common salt or Glaubersalt. The salts of the alkaline earths and of the heavy metals form lakes with cloth-red, thus rendering it possible to fix this dyestuff on metallic mordants. The lakes with calcium or magnesium salts are very little soluble in acetic acid; hence it is of little use to correct calcareous water with acetic acid; a purification by boiling up with sodium carbonate is preferable. The lakes are soluble in water containing 1 per cent. of tannic acid, which explains why the addition of sumach is advantageous when dyeing with hard water. Oxalic acid decomposes the calcium lake, forming calcium oxalate. Caustic alkalies do, but soap does not, readily precipitate the colour from solution.

Application.—Cloth-red is used in wool-dyeing and is fixed with the aid of chromium mordants, either alone or associated with tannin. It can also be dyed by the methods used for the acid colours, and thus yields a bluish-red shade. The great value of cloth-red, however, is based on the fastness of the colour both to light and to milling when dyed on chromium mordants. It is an excellent substitute for the red woods, as it combines well with the natural dyestuffs, *e.g.*, logwood or fustic, and can be saddened with copper and iron salts, giving rise to a variety of shades. The credit of having introduced this dyestuff as a fast mordant-colour is due to the firm of K. Oehler.

For the production of very fast colours the process of separate mordanting and dyeing is most satisfactory: Boil the wool for $1\frac{1}{2}$ to 2 hours with 3 per cent. of potassium bichromate and 3 per cent. of sulphuric acid or—for mixed shades in conjunction with wood colours—boil with 3 per cent. of bichromate, $1\frac{1}{2}$ per cent. of copper sulphate, and $1\frac{1}{2}$ to 3 per cent. of sulphuric acid. A smaller quantity of sulphuric acid produces shades which are not quite fast to milling. Deep shades require a greater quantity of mordant to resist milling perfectly, and for these the use of chromium fluoride is advisable, since an increased amount of bichromate might tender the fibre. Use 5 to 7 per cent. of chromium fluoride and half that amount of tartar or oxalic acid, and boil at least 2 hours. Compound shades with logwood cannot be produced with chromium fluoride alone; either some bichromate ($\frac{1}{2}$ to 1 per cent.) or some copper sulphate is required in addition.

After mordanting, the goods should be well rinsed in water.

For dyeing, no calcareous water should be used or some tannic acid or sumach should be added (see above). The dyestuff is dissolved in hot water and passed through a fine hair sieve into the dye-bath; for mixed shades the decoction of sumach, fustic, and logwood is boiled first and then the cloth-red is added. Light shades require the addi-

tion of a little ammonia or (for dyeing in copper vessels) of sodium acetate to the dye-bath to dye evenly and well through. For dark red shades the addition of 1 part of acetic acid to 1000 parts of water is of advantage, since it prevents too rapid dyeing. If a great quantity of dyestuff is required, only one-half is added at first and the rest after some time. The goods are introduced at 40°, the bath is gradually heated to the boiling point, and this temperature is maintained for about one hour; towards the end of the dyeing some acetic acid may be added to deepen the shade. The colour can be made faster to milling by adding 3 per cent. of stannic chloride to the exhausted dye-bath and boiling up. Wood colours which have been dyed in one bath with cloth-red can be saddened with iron or copper salts as usual. Alum must not be added to the bath, until the cloth-red is all taken up by the fibre, since this dyestuff is precipitated thereby. Fresh colour can be added even after the saddening and dyes evenly; but the dye-liquor should first be cooled down a little. Cloth-red G dyes on chrome-mordanted wool a full bluish-red shade, which is exceedingly fast to light and to milling; it is one of the fastest colours produced and well adapted for the production of a great variety of shades on loose wool or yarns that have to be milled in the piece.

Cloth-red can also be fixed in a single bath with chromium fluoride; for 1 part of colour 1 to 1½ parts of chromium fluoride are used *without* the addition of tartar. The method is useful for goods which do not require strong milling, but the colours of which require to be fast in wearing.

Cloth-red dyes in one bath with the addition of some tannin—*e.g.*, 5 per cent. of the weight of the wool of sumach extract (56° Tw.) The shades thus obtained are fast to light, but become bluer on milling; they can, however, be saddened with sulphate of copper or iron, and the effect of milling can thus be somewhat counteracted. Very dark claret-red shades are produced by the addition of logwood, and, if fustic is also added, a very fast brown will be obtained. Brown in one bath is produced by dyeing at the boil with sumach, fustic, and cloth-red for 1½ hours, cooling a little, adding sulphate of copper and boiling ¾ hour, cooling again, saddening with sulphate of iron, boiling ¾ hour, and finally washing. Black or grey shades, &c., can also be produced. In dyeing with cloth-red, either with chromium mordants or with tannin, concentrated baths should be used; else the colour will not be quite fast to milling; the mordanting bath must also be concentrated.

CLOTH-RED B (Oehler, M. L. B.)



Cloth-red B is analogous to cloth-red G in constitution, and is produced by the action of diazotised amidoazotoluene on betanaphthol disulphonic acid (R salt). It forms a brown-red powder, sparingly

soluble in water with a crimson colour; the aqueous solution yields a brown precipitate on addition of hydrochloric acid; caustic soda produces a claret-red precipitate soluble in pure water. The solution in sulphuric acid is blue, and gives a brown-red precipitate on diluting with water. In its general character, cloth-red B strongly resembles cloth-red G.

Application and Properties.—Same as cloth-red G. Cloth-red B produces a bluer and purer claret-red on wool.

CLOTH-RED B (Bayer).

Azo-dyestuff produced from amidoazotoluene and alphanaphthol monosulphonic acid N W, isomeric with cloth-red G (Oehler).

Brown powder, sparingly soluble in water; the aqueous solution is crimson-red; on addition of hydrochloric acid a red precipitate is obtained; caustic soda produces a soluble bluish-red precipitate. The solution in sulphuric acid is blue, and gives a crimson precipitate on diluting with water.

Application and Properties.—Same as cloth-red G.

CLOTH-RED 3 G (Bayer).

Azo-compound produced from amidoazotoluene and betanaphthylamine sulphonic acid Br, isomeric with cloth-red G (Oehler).

Brown-red powder, dissolving in water with a red colour; the aqueous solution gives a dark red-brown precipitate on addition of hydrochloric acid; caustic soda does not readily precipitate the colour. The solution in sulphuric acid is greenish-blue, and gives a dark red-brown precipitate on diluting with water.

Application and Properties.—Same as cloth-red G (Oehler).

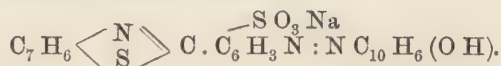
CLOTH-RED G (Bayer). AZO-COCCIN 7 B (Berlin).



This cloth-red G is different from the original cloth-red G introduced by K. Oehler. It is the azo-compound obtained from amidoazobenzene and alphanaphthol sulphonic acid N W, and forms a brown powder, which is not readily soluble in water. The aqueous solution is dark crimson, and yields a brown-red precipitate on addition of hydrochloric acid; caustic soda produces a soluble red-violet precipitate. The solution in sulphuric acid is blue, and yields a brown-red precipitate on diluting with water.

Application and Properties.—Same as cloth-red G (Oehler).

CLAYTON CLOTH-RED (Clayton).



Clayton cloth-red is the product of the reaction of diazotised dehydrothioparatoluidine sulphonic acid with betanaphthol.

The commercial product is a dark red granular powder which dissolves in hot water with a clear scarlet colour; hydrochloric acid produces an orange precipitate in the aqueous solution; caustic soda precipitates the dyestuff completely. In concentrated sulphuric acid it dissolves with a violet colour, and on diluting with water the dyestuff separates out as a red precipitate.

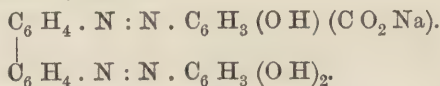
Application.—Clayton cloth-red can be dyed on wool as a direct acid colour, or on a chromium mordant in the same way as the preceding cloth-reds.

Dyeing without Mordants.—Enter the goods in the cold dye-bath acidulated with sulphuric acid or sodium bisulphate; heat very slowly up to the boil, and work until the bath is exhausted; the whole process should take $1\frac{1}{4}$ to $1\frac{1}{2}$ hours. Clayton cloth-red dyed in this way produces a full blue shade of scarlet, which is fairly fast to light; it bleeds slightly on milling, but does not go into the white.

Dyeing Mordanted Wool.—The goods are boiled $1\frac{1}{2}$ hours with 3 per cent. of potassium bichromate and 2 per cent. of sulphuric acid, rinsed in water, and entered into the cold neutral dye-bath; the liquor is heated to the boil, and the goods are worked until the bath is exhausted. Clayton cloth-red dyed with in this way is fast to milling; it does not differ much in appearance from the colour dyed without mordant.

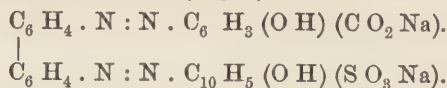
If desirable for the production of compound shades, the colour can also be dyed on wool which has been mordanted with 2 per cent. of bichromate, 2 per cent. of copper sulphate, and 2 per cent. of sulphuric acid.

CLOTH-ORANGE (Bayer).



Cloth-orange is an azo-compound produced by combining one molecule of diazotised benzidine with one molecule each of salicylic acid and of resorcin. It is a light chocolate-brown powder, which dissolves freely in water with a brown-orange colour; hydrochloric acid throws it down completely from the aqueous solution in the form of a brown precipitate, while caustic soda produces a soluble red precipitate. The solution in sulphuric acid is reddish-violet and yields a brown precipitate on diluting with water.

Application.—Cloth-orange dyes unmordanted cotton in an alkaline bath and unmordanted wool in an acid bath. It is used, however, on wool which has been mordanted with 3 per cent. of potassium bichromate and 1 per cent. of sulphuric acid, and acetic acid is added to the dye-bath. Cloth-orange dyes a brownish-orange shade, which is fairly fast to light and to milling; but the colour rubs off. The gradual addition of the acetic acid diminishes the rubbing.

CLOTH-BROWN, REDDISH (Bayer).

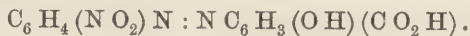
Cloth-brown (reddish) is produced analogously to cloth-orange, a naphthol sulphonic acid being used instead of resorcin. The colour forms a claret-brown powder, soluble in water with an orange-red colour; hydrochloric acid throws the colour down completely in the form of a scarlet precipitate; caustic soda produces a soluble red precipitate. The solution in sulphuric acid is red-violet and gives a red precipitate on diluting with water.

Application and Properties.—Same as cloth-orange. Cloth-brown (reddish) dyes a bright brick-red shade.

CLOTH-BROWN, YELLOWISH (Bayer).

Cloth-brown (yellowish) is produced similarly to the preceding two colouring matters, by combining benzidine with salicylic acid and a dioxynaphthalene. It forms a dark powder, which dissolves in water with a dark brown colour; the colour is thrown down from the aqueous solution in the form of a brown precipitate by hydrochloric acid; caustic soda colours the solution red-brown. The solution in sulphuric acid is dull reddish-violet and yields a brown precipitate on diluting with water.

Application and Properties.—Same as cloth-orange. The shade of cloth-brown (yellowish) is snuff-brown.

ALIZARIN-YELLOW G G (M. L. B.)

Alizarin-yellow G G is produced by the action of diazotised metanitriline on salicylic acid. It is sold as a light yellow powder, or as a yellow paste containing 20 per cent. of dry colouring matter; the former is readily soluble in water with a yellow colour, the latter is only slightly soluble. Both dissolve in caustic soda with an orange-red colour, but are precipitated by an excess in the form of a soluble yellow precipitate; hydrochloric acid produces in the solutions yellow precipitates. The solution in sulphuric acid is yellow, and yields on diluting with water a yellow precipitate. Alizarin-yellow G G shows considerable resistance to the action of oxidising agents, such as chlorine, chromic acid, &c., so that wool can be dyed with the same in conjunction with bichromates by the single-bath method.

Application.*—Alizarin-yellow G G serves as a substitute for Persian berries in calico-printing, and as a substitute for old fustic in wool dyeing. It produces a greenish-yellow shade on chromium mordants, and a beautiful golden yellow on alumina; but the former only is fast enough to soap to be employed.

* Nietzki, *Journ. Soc. Dyers and Col.*, 1889, p. 175.

Cotton.—Alizarin-yellow G G is dyed on cotton which has been mordanted with chromium oxide by any of the usual methods (p. 571). Chromium mordant G A I diluted with 3 to 4 times its weight of water is recommended by the makers; the goods are padded in this solution, dried, and passed, at 60°, through a solution of soda ash (6 parts in 1,000 of water); after washing, the goods are dyed in a bath containing acetic acid, starting cold and raising to 90°; it is advantageous to steam them for an hour after dyeing.

For dyeing on an aluminium mordant calcareous water is required.

Wool is dyed by the single-bath method with alizarin-yellow G G. 3 per cent. of bichromate and 1 per cent. of sulphuric acid are added to the dye-bath, the wool is introduced at 40° and the temperature is raised in $\frac{3}{4}$ hour to the boil and maintained so for 1 to 2 hours. An olive-yellow shade, similar to that of old fustic is obtained which is very fast to light and milling.

When the dyestuff has to be combined with alizarin-colours, &c., which do not give good results by the single-bath method, the wool is mordanted with 3 per cent. of bichromate and 1 per cent. of sulphuric acid, washed, and dyed as above; in this case any alkalinity of the bath is exactly corrected with acetic acid.

Alizarin-yellow G G can also be dyed on wool in an acid bath in the same way as the acid colours; it dyes evenly when thus applied, but has considerably less colouring power than on metallic mordants; the yellow shade is very fast to light.

ALIZARIN-YELLOW R (M. L. B.)

Alizarin-yellow R is isomeric with the preceding compound, being produced from paranitraniline and salicylic acid.

It forms a light brown paste containing 20 per cent. of dry colouring matter which is sparingly soluble in water; it dissolves with a deep red colouration in caustic soda solution, but is precipitated by an excess in the form of a soluble reddish-yellow precipitate; hydrochloric acid produces in the solution a brownish-yellow precipitate. The solution in sulphuric acid is red and yields a brownish-yellow precipitate on diluting with water.

Application and Properties.—Same as alizarin-yellow G G.

Alizarin-yellow R produces a full brown-orange shade on chromium mordants.

TERRA-COTTA R (Geigy).

Terra-cotta R is a nitrobenzeneazosalicylate of sodium produced by the action of nitric acid on the azo-compound which is prepared from diazobenzene chloride and salicylic acid.

Terra-cotta R is sold as a snuff-brown powder, soluble in water with an orange colour. Hydrochloric acid produces in this solution a dull orange precipitate, while caustic soda turns the solution orange-red.

The solution in strong sulphuric acid is amber-yellow and yields a dull orange precipitate on diluting with water.

Application.—Terra-cotta R is used in calico-printing and wool dyeing and can be applied in the same way as alizarin-yellow G G. It yields a pleasing shade of brown (terra-cotta).

MILLING-YELLOW (Dahl).



Milling-yellow (Dahl) is an azo-compound produced by the reaction of a diazotised betanaphthylamine-alphasulphonic acid with salicylic acid. The commercial article is a lemon-yellow powder, soluble in hot water; the addition of acetic acid makes the colour dissolve more rapidly.

Application.—Milling-yellow is used in wool dyeing. When dyed with the addition of 2 per cent. of sulphuric acid and 10 per cent. of Glaubersalt it yields a bright reddish-yellow shade (similar to that obtained with tartrazin) which resists light and milling exceedingly well and is fast to acids. Dyed on wool mordanted with bichromate and sulphuric acid, or with chromium fluoride, it yields shades which are similar to old fustic, but redder; they are extremely fast to light and milling and fairly fast to stoving. This dyestuff can also be used with potassium bichromate by the single-bath method.

DIAMOND-YELLOW G (Bayer).



Diamond-yellow G is produced by combining diazotised meta-amido-benzoic acid with salicylic acid. It is sold as a greyish-yellow paste, which dissolves sparingly with a yellow colour in water, but is readily soluble in a solution of soda or of sodium acetate; hydrochloric acid produces a yellow precipitate in the alkaline solutions. The solution in sulphuric acid is reddish-yellow, and gives, on diluting with water, a yellow gelatinous precipitate.

Application.—Diamond-yellow G is used in the same way as the preceding yellow colouring matters as a fustic substitute for the dyeing of wool mordanted with chromium mordants. It combines well with other mordant colours. Dyed alone, diamond-yellow G yields very fast shades resembling old fustic.

DIAMOND-YELLOW R (Bayer).

Diamond-yellow R is isomeric with diamond-yellow G and is produced from orthoamidobenzoic acid and salicylic acid. It forms a brown paste, little soluble in water with a yellow colour, readily soluble in a solution of sodium acetate or soda. The solution in sulphuric acid is reddish-yellow; on diluting a brownish-yellow precipitate is obtained.

Application and Properties.—Same as diamond-yellow G. It dyes a redder shade.

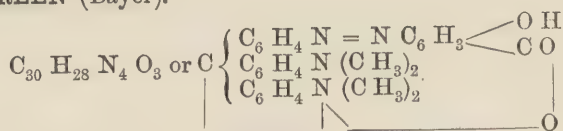
PATENT-FUSTIN (Wood & Bedford). **WOOL-YELLOW** (B.A.S.F.)

Patent-fustin or wool-yellow is the product of the reaction of diazobenzene on the colouring matter of old fustic. Similar but redder colours are produced analogously with diazotoluene and diazoxylene. The commercial article is a brown-yellow powder or brown-yellow paste, almost insoluble in water; it dissolves in caustic soda with a yellow-brown colour and is precipitated from this solution by hydrochloric acid. The solution in sulphuric acid is yellow-brown and yields a brown-yellow precipitate on diluting with water.

Application.—Patent-fustin is dyed on mordanted wool in the same way as old fustic. It dyes evenly and possesses the advantage over fustic that it gives uniform results. It can be used along with the wood-colours, alizarins, and other dyestuffs which are fixed on metallic mordants. The saddening with iron mordants is not quite satisfactory in this case, as the effects produced are somewhat variable.

Patent fustin dyes on chrome-mordanted wool a brown-yellow shade fairly fast to light and to milling and very fast to stoving. The shade is not equal to fustic in fastness to light; it becomes a little lighter by strong milling, but it does not tinge adjacent white. Patent-fustin may replace fustic for modes, but is not so well adapted for shades, such as green, for instance, which require a pure and full yellow.

A purer yellow shade is produced on aluminium mordants, but it is not fast to milling.

AZO-GREEN (Bayer).

Azo-green is a derivative of triphenylmethane and is an azo-compound. For its production meta-amidotetramethylparadiamidotriphenylmethane is diazotised and combined with salicylic acid; the leuco-compound thus obtained is transformed into azo-green by oxidation. The above-named base is produced by the condensation of metanitrobenzaldehyde and dimethylaniline and subsequent reduction of the nitro-compound. Azo-green owes its green colour to the triphenylmethane group; the azo-group cannot be considered as the chromophor of this colouring matter. Azo-green is sold as a dark green paste, sparingly soluble in water with a green colour. The paste when suspended in water becomes brown-red on the addition of hydrochloric acid; caustic soda in the cold has no action; on heating, the colour dissolves slowly; the cold alkaline solution is not precipitated by hydrochloric acid; but, on heating, a brown-red precipitate is formed. The solution in sulphuric acid is brown-yellow and gives a reddish precipitate on diluting with water.

Application.—Azo-green is dyed on chrome-mordanted wool (3 per cent. of bichromate and 1 per cent. of oxalic acid). Enter at 30°, heat slowly to the boil and boil for $\frac{3}{4}$ hour; the bath is not exhausted; after dyeing, rinse in water containing 1 part of soap in 1000 parts. The shade is a full green, moderately fast to light, and fairly fast to milling, but not to rubbing.

Silk is dyed with the addition of 2 per cent. of acetic acid, **Jute** without any additions.

DIAMOND-GREEN (Bayer).

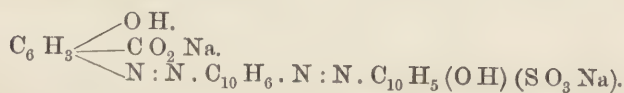
Diamond-green is a new dyestuff of unknown composition. It resembles diamond-black in constitution and general character.

Application.—Diamond-green is used for wool dyeing; it can also be fixed on silk, but not on the vegetable fibres. It dyes evenly and combines well with the alizarins, wood-colours, &c., and particularly well with diamond-black.

When dyed on wool with the addition of Glaubersalt only it produces a black colour with a blue bloom, which can be made greenish-black by boiling for half an hour in a solution of 2 per cent. of potassium bichromate (of the weight of the wool). The dye-bath is not exhausted and should be used continuously; the process has the advantage of dyeing very evenly and well through. A dark "Russian" green shade is produced on wool which has been mordanted with 3 per cent. of bichromate and 1 per cent. of oxalic acid. Enter at 40°, raise slowly to the boil and boil for one hour, wash, and dry.

Diamond-green is very fast to light, milling, rubbing, stoving, acids, and alkalies.

DIAMOND-BLACK (Bayer).



For the production of diamond-black amidosalicylic acid is diazotised and combined with alphanaphthylamine; the product is rediazotised and combined with alphanaphtholsulphonic acid N W. The dyestuff forms a black-blue powder, which dissolves in water with a blue-violet colour; hydrochloric acid produces a violet precipitate in the aqueous solution; caustic soda turns the solution blue. The solution in sulphuric acid is green and yields a violet precipitate on diluting with water.

Application and Properties.—Same as diamond-green. Diamond-black can also be dyed in a boiling bath with the addition of nitrate of iron. When dyed without mordants it yields a black-violet shade, on chromium mordants a violet-black, which can be shaded to jet-black by diamond-green. Diamond-black dyes well through and is very fast to light, milling, rubbing, stoving, acids, and alkalies.

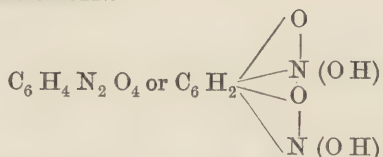
NITROSO-COMPOUNDS.

By the action of nitrous acid on certain phenols compounds are obtained which are frequently called nitroso-phenols, the correct name of which, however, is "quinoneoxime," since they do not contain the nitroso-group N O , but the quinoneoxime-group $\left\{ \begin{smallmatrix} \text{O} \\ \text{N O H} \end{smallmatrix} \right.$. The orthoquinoneoximes dye on metallic mordants, according to St. Kostanecki,* while the other quinoneoximes do not. The combination of

atoms $\begin{array}{c} \text{C} \text{---} \text{O} \\ | \quad | \\ \text{C} \text{---} \text{N} (\text{O H}) \end{array}$ acts both as a chromophorous and as an auxochromous group. These colours are permanently decolorised by the action of reducing agents, amidophenols being formed.

The nitroso-compounds are dyed almost exclusively on iron mordants, and invariably produce with this metal green shades, which are distinguished by fastness to light. Cobalt mordants yield handsome browns.

DINITROSO-RESORCIN.



Chlorin. Fast Green. Dark Green. Russian Green. Alsace-Green.

Dinitroso-resorcin forms a grey powder, sparingly soluble in cold, but more soluble in hot water. It forms two classes of salts; the acid salts with one equivalent of alkali are crystalline and sparingly soluble in water; the neutral salts with two equivalents of alkali are readily soluble in water. The ferric salt is dark green.

The commercial product is sold as a dark grey paste (the dry powder being explosive), which dissolves in water with an olive-yellow colour. Hydrochloric acid has no action on the solution; caustic soda makes it darker. The solution in sulphuric acid is pale yellow, and becomes lighter on being diluted with water.

Application.—Dinitroso-resorcin is chiefly used in dyeing cotton piece goods. The material is mordanted by pyrolignite by padding, ageing, and fixing with silicate of soda and chalk; then, after being washed in water, it is dyed in a neutral bath or in one which has been very slightly acidified with acetic acid (to neutralise lime), entered at the ordinary temperature, heated in 45 minutes to the boil, washed, and dried. Dinitroso-resorcin dyes a dark olive-green, fairly fast to light and moderately fast to soap.

H. Koechlin has produced on calico a fine brown with the aid of a cobalt mordant by printing a paste prepared with 29 grms. of cobalt

* *Journ. Soc. of Dyers and Col.*, 1888, p. 7.

nitrate, 25 grms. of sodium acetate, and 1 litre of tragacanth size, passing through aluminate of soda at 30° C. and dyeing in a bath containing 5 grms. of dinitroso-resorcin and 6 grms. of a solution of calcium chloride (32° Tw.) per metre of calico.

The green and brown colours can be produced on wool or silk by similar processes.

ESSAÏN.

Essaïn is a new brown colouring matter obtained from dinitroso-resorcin. According to H. Schäffer* and F. Binder,* for the production of essaïn

350 grms. dinitroso-resorcin paste (50 per cent.),
255 cc. hydrosulphite of sodium, and
312 cc. water

are mixed. The hydrosulphite is prepared by reducing 700 cc. of sodium bisulphite (82° Tw.) with 200 grms. of zinc dust. At first the reaction is slow, but it soon becomes more active, and a considerable amount of froth is formed; the reaction lasts about two hours and a half (during which time the mixture must be stirred to regulate the action of the reducing agent) and the temperature rises to 58°. After cooling, the colouring matter is filtered, and is obtained as a perfectly clear brownish-red liquid which mixes in any proportion with water or acetic acid.

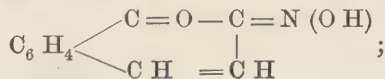
Application.—Essaïn seems to be used in the United States for calico-printing. It can also serve for wool printing and wool dyeing. It produces pure reddish-brown shades, fast to soap, acids, and alkalies, but especially to light.

It is fixed by means of chromium mordants. Wool is mordanted with bichromate and dyed in a fresh bath with essaïn with the addition of some oxalic acid (*Schäffer*). About 8 per cent. of the colouring matter produces an average brown.

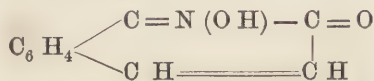
NITROSO-NAPHTHOL. $C_{10}H_7NO_2$.

Gambin R and Y (Holliday). Alsace-Green J (Thann).

Two isomeric compounds of very similar properties are in the market which are produced by the action of nitrous acid on alphanaphthol and betanaphthol respectively. Both are *naphthoquinoneoximes*. Nitroso-alphanaphthol (gambin R), the product of alphanaphthol, is



nitroso-betanaphthol (gambin Y) is



* *Journ. Soc. Dyers and Col.*, 1891, p. 138.

They form greenish-brown pastes, sparingly soluble in water. The aqueous solution is not affected by hydrochloric acid; in caustic soda the colours dissolve freely with a yellow colour. The solutions in sulphuric acid are brown and yield brown precipitates on diluting with water.

Application.—The nitroso-naphthols are principally used in calico-printing and in wool dyeing. They produce with iron mordants olive-greens, approaching the shades obtained by dinitroso-resorcin; with chromium mordants, cutch shades; with nickel salts they produce bronzes; with cobalt, cutch-browns; with cerium salts, bronzes with a brown tinge; with uranium, yellows. The shades obtained by nitroso-alphanaphthol are in general darker than those obtained by nitroso-betanaphthol.* The nitroso-naphthols may be used for dyeing cotton or wool, producing with the usual mordants shades which are very fast to light and soap. For printing, their application is more difficult, because they appear to be volatilised and, perhaps, to decompose on steaming.

The colour should be well mixed with 3 or 4 times its weight of cold water before being added to the dye-bath; wooden vessels should be used, as iron in any form tends to green the shades produced.

Cotton is dyed by exactly the same method as with dinitroso-resorcin.

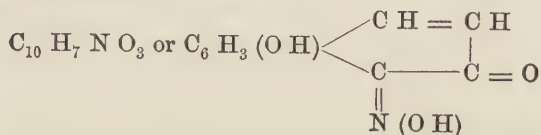
Wool.—*Browns* are produced by previously mordanting the wool with potassium bichromate with, or without, the addition of tartar or sulphuric acid; the latter makes the shade redder. For a full shade, up to 30 per cent. of nitroso-naphthol are required. Add the colour to the lukewarm bath, enter the goods, heat slowly to the boil and boil for half an hour or more.

Olive shades are obtained by proceeding in the above manner and then saddening to the required shade with ferrous sulphate; the longer the material remains in this bath and the more copperas there is used, the greener is the shade.

Green.—Mordant with 3 per cent. of ferrous sulphate and 1 to 3 per cent. of tartar, wash and dye in a fresh bath with nitroso-naphthol in the same manner as for brown; if the wool is afterwards boiled with bichromate the shade can be turned to an olive.

The nitroso-naphthols combine well with the wood-colours, alizarins, and other mordant-colours. The colours on iron mordants are extremely fast to light, those on chromium mordants not quite so, although very fast in full shades.

DIOXIN (Leonhardt).

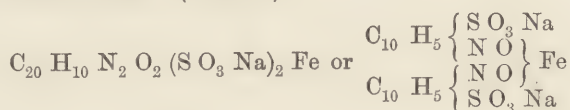


* Ed. Koechlin, *Journ. Soc. Dyers and Col.*, 1891, p. 137.

Dioxin is the product of the reaction of nitrous acid on (2 : 7) dioxy-naphthalene. It forms a brown paste, which is sparingly soluble in water with a brown colour. It dissolves in caustic soda with an intense brown-red colour, and is precipitated from this solution by hydrochloric acid. It dissolves in sulphuric acid with a bright green colour; this solution yields a red-brown precipitate on diluting with water.

Application.—Dioxin is dyed on wool either with an iron mordant (copperas and oxalic acid or tartar) or with a chrome mordant by the methods given for nitroso-naphthol. It yields with iron a yellowish-green which is brightened by milling; with chrome it produces a brown which is not fast to milling, but does not bleed into the white; on wool mordanted with mixtures of chrome and iron compound shades may be produced. The various shades resist the action of light well.

NAPHTHOL-GREEN (Cassella).



Naphthol-green may be considered to be an iron-compound of a sodium sulphonate of nitroso-betanaphthol. It is produced by the action of nitrous acid on betanaphtholsulphonic acid (Schäffer) and by mixing the product of this reaction with ferric chloride. The iron is in intimate combination with the organic compound and cannot be readily detected by the usual means; if the substance is heated on platinum foil, ferrous sulphide is obtained.

Naphthol-green is a dark green powder, freely soluble in water, with a dark yellowish-green colour. The aqueous solution is not changed in the cold by hydrochloric acid, but becomes yellow when heated with this reagent, and yields blue precipitates with yellow or red prussiate. Caustic soda does not change the colour of the solution. The solution in sulphuric acid is brownish-yellow; it becomes yellow on diluting, and then it shows the iron reaction with the prussiates.

Application.—Naphthol-green is dyed on unmordanted wool and silk. This dyestuff is placed with the mordant-colours on account of its relations to the four preceding compounds and because it may be considered to be a mordant-colour which already contains the metallic constituent and is dyed by the single-bath method.

Wool is dyed in an acidulated bath with the addition of some copperas; for a full shade about 5 per cent. of naphthol-green, 5 to 10 per cent. of copperas, and 2 per cent. of sulphuric acid are required. The goods are entered cold and the temperature is slowly raised to the boil. Naphthol-green dyes an olive-green; it is distinguished by fastness to light and is fairly fast to milling, but is deteriorated by the

action of soda. It is suitable for mixtures with dyestuffs which are dyed in an acid bath.

Silk. Naphthol-green may be dyed on silk with the addition of tartaric acid.

MISCELLANEOUS COLOURS.

The colours described under this heading have little similarity, chemically or tinctorially, either amongst themselves or with the preceding dyestuffs. They are not soluble in the ordinary solvents, and are produced in the fibre by peculiar processes; but canarin is a partial exception, since it can be fixed as canarin on the fibre from a solution of borax or be produced on the material by oxidation of thiocyanates.

ANILINE-BLACK.*

Aniline-black is produced by the oxidation of aniline. Runge, as early as 1834, noticed the mode of formation of this body and produced it on the fibre. Fritzsche and others afterwards studied this substance; but it did not obtain commercial importance until soon after 1860, when aniline could be bought in quantities at a reasonable price. The composition of aniline-black is not known; it is produced by the action of oxidising agents on aniline and homologous bases, and the products vary to some extent according to the methods of operation. Three different compounds are distinguished as products of oxidation of pure aniline:—

- (1) Emeraldine (Azurine).
- (2) Nigraniline.
- (3) Ungreenable Black.

Emeraldine is the first product of oxidation; it is a green-coloured salt, the base of which in the free state is blue and is called *Azurine*. This substance is somewhat soluble in alcohol, glacial acetic acid, &c., and dissolves in concentrated sulphuric acid with a violet-red colour. Emeraldine is probably identical with compounds which have been produced by a moderate oxidation of equal molecules of paraphenylenediamine and diphenylamine or of para-amidodiphenylamine and aniline or by oxidation of aniline in the free state by means of potassium permanganate. The composition of emeraldine is not known; probably it has never been prepared in the pure state, but always mixed with nigraniline.

Nigraniline is formed by the oxidation of emeraldine; the composition of this substance is expressed by the formula $(C_6H_5N)_n$, various multiples of C_6H_5N from $C_{12}H_{10}N_2$ to $C_{30}H_{25}N_5$ having been given as the correct formula. The base itself has a violet-black colour, while its salts are dark green. It is insoluble in the ordinary solvents, but is slightly soluble in aniline or phenol.

* E. Noelting, *Histoire scientifique et industrielle du noir d'aniline*. Mulhouse. 1889.

Nigraniline dissolves in strong sulphuric acid with a violet colour and is thus converted into sulphonic acids, the alkali-salts of which are soluble in water. The aqueous solutions of the salts are decolorised by reducing agents (such as hydrosulphite or zinc and caustic soda) and transformed into leuco-compounds, which are rapidly reconverted into the original substance on exposure to the air. The same sulphonic acids are formed by the oxidation of aniline with potassium bichromate in the presence of concentrated sulphuric acid.

Nigraniline is converted by energetic oxidation with potassium bichromate and sulphuric acid into quinone; and by energetic reduction with hydriodic acid and phosphorus into paraphenylenediamine and diamidodiphenylamine. It contains several atoms of hydrogen replaceable by the groups methyl, acetyl, &c.; on being boiled with aniline it yields a blue substance, which seems to be an induline and probably has the composition $C_{36}H_{29}N_5$. The behaviour of nigraniline towards moderate reducing and oxidising agents is most important for the practical application of aniline-black. Nigraniline becomes green under the influence of acids, especially of sulphurous acid, which change of colour is probably caused by a partial or entire reduction of the compound to emeraldine; the well known "greening" of aniline-black is due to this cause. By a moderate oxidation nigraniline is converted into ungreenable black.

Ungreenable Black is formed by the action of oxidising agents on nigraniline at an elevated, and, under certain conditions, at the ordinary temperature. It forms a black mass, and does not become green under the influence of acids, probably because it is not capable of forming salts, nor is it turned green by sulphurous acid. It is reduced by stannous chloride to a leuco-compound, from which the black is regenerated on exposure to the air. The ungreenable black contains oxygen, and combines with metallic oxides, such as chromic oxide.

An aniline-black obtained by the action of potassium bichromate on nigraniline is turned green by sulphurous acid, but not by other acids. It is probably a chromate of nigraniline.

Nigraniline and the ungreenable black are the chief constituents of the aniline-black in the fibre. The process by which these compounds are formed has not been satisfactorily explained. Chloric acid does not readily transform aniline into black; a solution of aniline chlorate can be boiled without being decomposed; but the black is formed as soon as a drop of acid is added, or in presence of a very small amount of a metallic salt, the chlorate of which is readily decomposed—*e.g.*, salts of vanadium, cerium, copper, manganese, or iron. The chloric acid is decomposed under these conditions, and the products of reduction oxidise the aniline. It has been supposed that the presence of a metal which is able to form more than one oxide is required to produce aniline-black, and that the chlorate acts indirectly on the aniline, the metallic oxide acting as the carrier of oxygen. It has been shown, however, that aniline-black can be produced with the oxides of chlorine without the

intervention of metals, and that the latter merely serve to reduce the chloric acid into the lower oxides of chlorine, which act directly on the aniline. Noelting believes that both reactions can take place simultaneously.

The bichromate of aniline resembles the chlorate in stability; and the black is formed immediately, if acid is added to the solution.

The action of several "reserves" in printing is based on the fact that no black is formed in the absence of acids.

Aniline-black is changed to green by acids, especially sulphurous acid, if the colour has not been already converted into "ungreenable black" by oxidation. The purer the aniline-oil is from which the aniline-black is prepared the more strongly does this objectionable property manifest itself. Those blacks which are obtained from aniline-oil containing toluidines and xylidines are comparatively free from it; hence it is that while improvements in manufacture have produced a purer aniline-oil, the complaints about "greening" have increased. The less pure anilines, however, do not yield such a fine black as the pure product. Orthotoluidine produces a black with a violet hue which is less blue than that from pure aniline, but nevertheless very fine; this black does not turn green so easily as aniline-black. Paratoluidine and commercial xylidine furnish browns. The colour which is produced with xylidine is a dark olive-brown, and is turned to a more yellowish shade by acids and sodium bisulphite; paratoluidine yields a more yellowish-brown, which is less sensitive to acids than that from xylidine. The commercial toluidine, a mixture of the two isomers, produces a black of a fair shade, which is faster as regards "greening" than that from aniline. These results were obtained by Prudhomme,* in accordance with whose investigations a method was patented in 1879† for producing an ungreenable aniline-black by a single oxidation. For this purpose 100 parts of liquid toluidine, containing 60 to 70 parts of orthotoluidine, are mixed with 30 to 40 parts commercial xylidine, and the resulting oil is used like the ordinary aniline-oil (oil for blue, &c.).

Aniline-Black or *Nigraniline*, produced by oxidation of aniline (not on the fibre), is a violet-black powder which forms dark green salts. It is insoluble in the ordinary solvents, but dissolves in aniline-oil with a violet colour (which soon becomes brown), and in phenol with a blue-green colour; it dissolves in strong sulphuric acid with a violet colour; on diluting with water the solution yields the sulphate as a dark green precipitate.

Aniline-black is sold as a black paste, which is sometimes used as a steam black in printing; the colour is thickened with albumen and fixed by steaming.

Application.—Aniline-black is extensively employed in cotton

* *Journ. Soc. Dyers and Col.*, 1891, p. 71.

† British Patent, 1879, No. 3101.

dyeing and calico-printing. It is, however, not often applied as aniline-black (never in dyeing, rarely in printing), because it can neither be rendered soluble nor fixed on the fibre like other colours. The only practical method of dyeing with it is to produce the black direct in the fibre, which can easily be done on cotton (loose cotton, yarn, or piece goods). The dyeing with aniline-black on this fibre is of great importance, and it has superseded to a great extent the blacks formerly produced with logwood. This is chiefly due to the extraordinary fastness of the colour which yields a fine jet-black, fast to light, soap, alkalies, chloring, and, when dyed in the right way, also to acids (sulphurous acid especially) and to rubbing.

The principal disadvantage in dyeing with aniline-black is the weakening influence of the acids and oxidising agents on the fibre; this, however, can be almost entirely prevented by carefully regulating the process.

The application of aniline-black to wool and silk offers difficulties, owing to the reducing action exerted by animal fibres; chlorinating the material before dyeing has been tried, but the feel, lustre, and tenacity of the fibres are injured by the preparing and dyeing process. The animal fibres are very rarely dyed with aniline-black, and the methods employed are kept secret.

The most usual oxidising agent employed for *dyeing* aniline-black on loose cotton and cotton yarn is bichromate of potash, or better, bichromate of soda, as it is both cheaper and more soluble. The method was patented by Boboeuf in 1865, and is still used in France in the following form for yarn dyeing (*Noelting*). Two separate solutions are prepared—one with 6 kgs. (6 lbs.) of aniline, 9 kgs. (9 lbs.) of hydrochloric acid, and 12 kgs. (12 lbs.) of sulphuric acid in 200 litres (20 galls.) of water; the other with 12 kgs. (12 lbs.) of bichromate of soda, and 200 litres (20 galls.) of water. After allowing to cool, 2 litres (4 quarts) of either solution are poured into a small dish, and the yarn is rapidly passed through this bath in lots of 1 kg. (2 lbs.); within one or two minutes a bronze-black is developed. The material is then wrung out and steamed for 20 minutes at $3\frac{1}{2}$ pounds pressure. The bronze-black becomes jet-black, and is rendered practically ungreenable by the steaming. The hanks are finally washed and soaped at the boil. For the soaping (which is generally required after the dyeing of aniline-blacks) a solution of 5 to 10 parts of oily soap per 1000 parts of water (with or without the addition of sodium carbonate) is used. The utility of the steaming is based on the fact that a black oxidised at an elevated temperature does not turn green so soon as those obtained at lower temperatures. Hydrochloric and sulphuric acid are used together to obtain a jet-black, since the former alone produces a bluish- and the latter a reddish-black. The following proportions have also been recommended (*A. Renard*) for 100 kgs. (lbs.) of cotton:—

8 to 10 kgs. (lbs.) aniline,	14 to 20 kgs. (lbs.) bichromate, and
16 to 20 kgs. (lbs.) hydrochloric acid,	10 kgs. (lbs.) ferrous sulphate,
20 kgs. (lbs.) sulphuric acid,	

dissolved in a sufficiency of water.

In this case the ferrous salt is oxidised by the bichromate, and acts as a carrier of oxygen.

The oxidation of the aniline may also take place at an elevated temperature. This method has the disadvantage that much of the black is formed on the surface only, or away from the fibre, especially if there is an excess of acid, and that the colour is liable to rub badly. To avoid this drawback, the reaction is moderated by diluting the bath considerably; and by reducing the proportions of the acid and the bichromate. A. Renard recommends about the following proportions for 100 kgs. (100 lbs.) of cotton:—

10 kgs. (10 lbs.) aniline-oil,	40 kgs. (lbs.) hydrochloric acid, and
15 kgs. (15 lbs.) bichromate,	1,600 litres (160 galls.) water.

or 12 kgs. (12 lbs.) hydrochloric acid only, and in addition 6.4 kgs. (6.4 lbs.) sulphuric acid.

The proportions vary according to the desired shade of black; the finest and most permanent blacks are obtained with the largest amounts of aniline; the quantity of water given here seems excessively large.

The dye-bath is filled with water and the cold solution of aniline-oil and a part of the hydrochloric acid in water is first added, afterwards the bichromate dissolved in a small quantity of water, and the remainder of the acid last; sometimes only one-half of the chemicals is added to the bath at the beginning, and the other half after one hour's turning. The cotton is introduced into the cold bath and turned continuously; when the colour becomes distinct, the bath is slowly heated to 50° or 60° to develop the shade; the material has at first a greyish-green tone, which passes gradually through deep green to black. The operation may last from one to three hours, according as the bath is more or less concentrated or acid; if, however, the heating has been of too short a duration, the black is liable to turn green under the influence of acids.

It has already been stated that aniline-black produced at a temperature above 75° does not turn green so soon; blacks which have been obtained at lower temperatures are easily made ungreenable by a second oxidation above 75°.

According to Koechlin Brothers the readily decomposable ferric salts, chromic acid, and chlorates, give the best results. The ferric solution is prepared with a ferric salt, to which one to one and a half times its weight of sulphuric acid has been added for the purpose of preventing the fixation of ferric oxide on the fibre; of this solution 1 to 2 parts (by weight) are diluted with 1,000 parts of water. As copperas is cheaper than ferric salts, it is recommended to prepare the ferric solution by dissolving:

20 kgs. (20 lbs.) of ferrous sulphate in
 60 to 70 litres (6 to 7 galls.) of water, and adding
 5 kgs. (5 lbs.) of bichromate and
 15 to 18 litres ($1\frac{1}{2}$ to $1\frac{3}{4}$ galls.) of concentrated sulphuric acid.

One part (by volume) of this solution is diluted with 100 parts of water. The dyed cotton is worked in the resulting liquor at 80° for 30 to 60 minutes, then washed and soaped as before. A solution of 1 part of bichromate in 1000 parts of water to which an equivalent amount of sulphuric acid is added can be used in the same way.

For dyeing aniline-black on cotton piece goods, sodium chlorate is generally used (the sodium salt being preferable to the potassium salt on account of its greater solubility). Crace-Calvert, Clift, and Lowe, as early as 1860, described a method for producing an aniline-black on calico by means of potassium chlorate. In 1863, J. Lightfoot invented a great improvement of their method by adding cupric chloride to the colour; the function of this salt, which reduces the chloric acid to a lower oxide of chlorine, and possibly acts as a carrier of oxygen, has been discussed above. Cupric chloride greatly facilitates the oxidation of aniline and the production of a good black. It has, however, the great drawback in printing that it attacks the doctors and rollers of the printing machines, and that it causes a premature oxidation of the aniline in the prepared colour on standing. These obstacles were overcome by Ch. Lauth and C. Koechlin. Lauth replaced the cupric salt of Lightfoot by cupric sulphide, which is oxidised on the fibre in moist air to form cupric sulphate, thus acting gradually and at the desired moment only. Koechlin used a mixture of aniline tartrate and ammonium chloride for delicate fabrics to prevent the fibre from being tendered; the tartrate does not by itself yield a black, but it and the ammonium chloride gradually act on each other, and form the hydrochloride in such proportions as not to attack the fibre; the process is valuable for calico-printing. Koechlin also recommended that the expensive tartrate be replaced by a basic aniline hydrochloride (*i.e.*, an aniline hydrochloride, to which some aniline-oil is added). The more acid the mixture is the more rapidly is the colour developed, and the greater is its weakening action on the fibre; on the other hand, if the mixture is too basic, no colour is produced; the mixture should be neither too acid nor too basic. The following recipe was given by Koechlin:—

Dissolve 10 parts potassium chlorate,
 10 parts ammonium chloride,
 10 parts copper chloride,
 20 parts aniline-oil,
 20 parts hydrochloric acid, in
 200 to 300 parts water.

Impregnate the material with this solution, age at a low temperature, and wash after 24 hours. The difficulty in carrying out this recipe lies in the small solubility of potassium chlorate. If 300 parts

of water are used no full black is obtained; if only 200 parts of water are employed the formation of the black proceeds too rapidly and partially on the surface of or away from the fibre, and the colour obtained rubs. Wh. Evans* recommends the following modification of Koechlin's method to avoid rubbing:—

10 parts chlorate of soda,
10 parts ammonium chloride,
10 parts copper sulphate,
35 parts aniline-salt,
 x parts aniline-oil,
200 parts water.

The sodium chlorate (10 parts) and ammonium chloride (10 parts) are dissolved in water (65 parts); and the copper sulphate (10 parts) separately in water (55 parts). The aniline salt (which should be as white as possible) is dissolved in as little hot water as possible and neutralised with a sufficient amount of aniline-oil (x parts). The various substances are dissolved the day before they are used, so that the solutions have ample time to cool. The solution of the aniline salt is first added to that of the sodium chlorate and ammonium chloride; after which the copper solution is added; the whole is diluted with water until it has a specific gravity of 14° Tw. The use of thickenings must be avoided.

The material to be dyed is now impregnated two or three times with this colour, excess of liquor is removed by hydro-extracting and then follows the ageing, preferably in the "Mather & Platt" (see below). After 10 pieces have passed through the colour solution, the latter is replaced by fresh liquor; especially in summer caution is required, since the increased temperature of the air greatly facilitates the formation of black in the solution (away from the fibre). The liquors are not thrown away, but filtered and used over again for diluting fresh colour. The material is fully aged when exposed for 14 hours to an atmosphere having a temperature of 30° C. by the dry and 25° C. by the wet bulb thermometer. For their further treatment the goods are treated at 80° in a solution containing 10 parts of bichromate, 5 parts of soda, and 5 parts of common salt per 1,000 parts of water, after which they are washed lukewarm without soap and dry-steamed at a pressure of 15 pounds.

In fig. 58 is shown the steaming apparatus of *Mather & Platt*, which is now very generally used for the development of aniline-black instead of ageing in the air. The machine consists of a spacious chamber, which is fitted with a number of copper rollers to guide the pieces while passing through the chamber. In the drawing the wall is cut out on one side to show the arrangement of the rollers. The pieces pass into the upper part through a small slit and come out through the same opening after having been run through the whole apparatus. Two copper

* *Journ. Soc. Dyers and Col.*, 1891, p. 20.

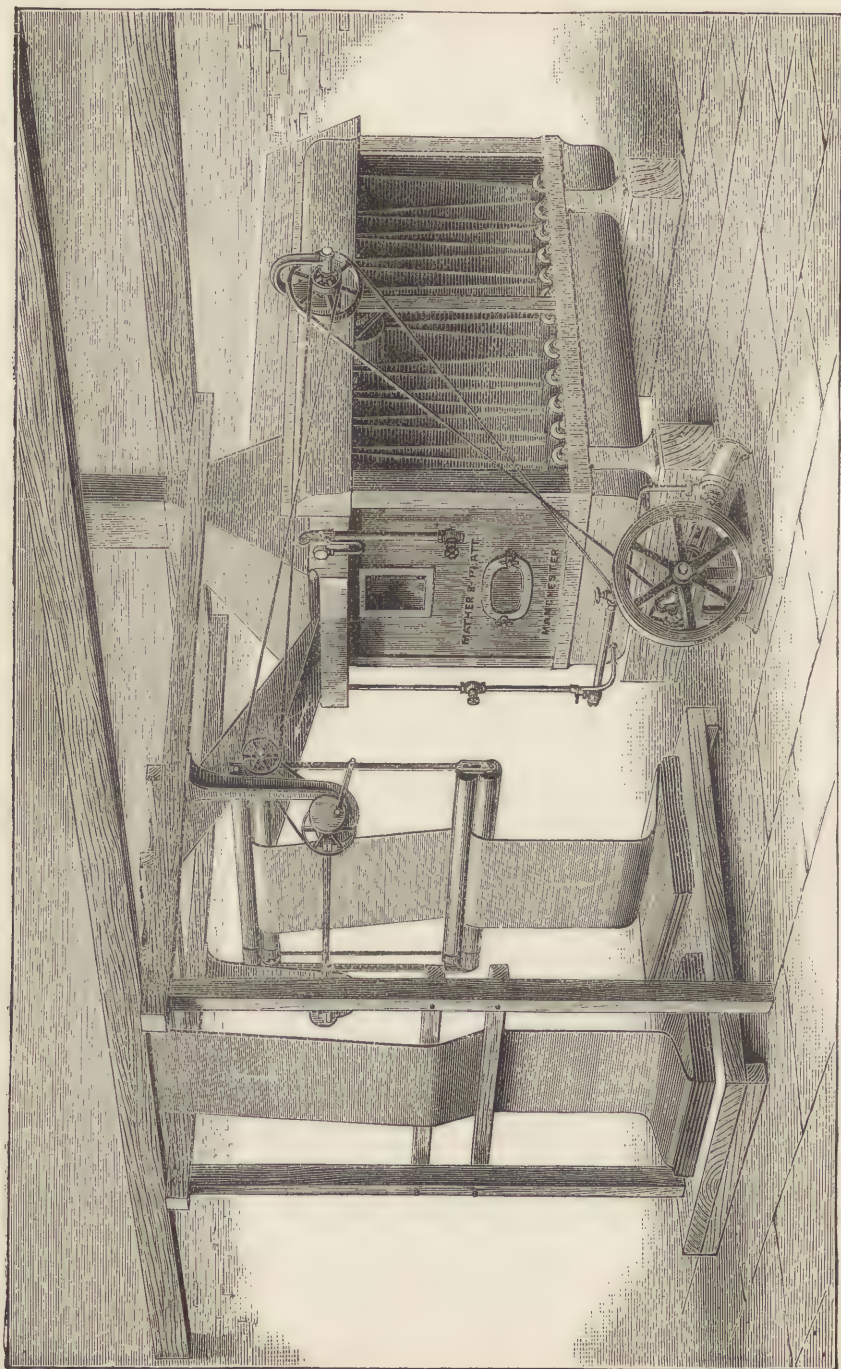


Fig. 58.—Mather & Platt's ageing machine.

tubes are fitted near the opening and heated by steam to prevent the water from condensing; for the same purpose the cast-iron roof is constructed hollow and heated by steam. The steam which has been used to heat the roof and copper pipes serves for supplying the interior with steam; if necessary, steam can be directly injected by means of a perforated pipe which is fixed on the bottom of the chamber. A manhole is fitted on one end. The temperature is shown by a thermometer, which is placed in the chamber behind a glass plate. The pieces pass through the apparatus at the rate of about 60 to 100 yards per minute.

A. Kertecz* has put forward the theory that the absence of free mineral acids is essential for the production of an ungreenable steam-aniline-black. Frequently potassium ferrocyanide is added to the dye-liquor, and this author explains the formation of ungreenable aniline-black in the presence of this salt by the fact of its neutralising the mineral acid and forming aniline ferrocyanide; whether the alkaline ferrocyanide acts only by neutralisation or whether it assists in the formation of an ungreenable black by yielding Prussian blue on steaming the author does not decide. The same author has expressed very recently the opinion that it is owing to a difference of the depth of shade whether a black will turn green or not, and that the blacks produced with yellow prussiate are more permanent on account of the greater depth of colour they possess.

Excellent results are obtained by working in the following way:—
Prepare concentrated solutions of

1·8 parts of aniline salt,
12 parts ferrocyanide of potash,
3½ parts potassium chlorate
in water;

work in a jigger with this solution; steam in the Mather & Platt apparatus for two minutes; work hot in a jigger in a solution of 1 part of bichromate per 500 parts of water, dry, and finish.

A great number of salts have been recommended in place of copper compounds to facilitate the action of the chlorate on the aniline and to produce a good black. At an early date it was proposed to precipitate insoluble chromates (such as those of copper or lead) in the fibre; later, the copper sulphide was replaced by cuprous sulphocyanide, which is still used under the name of "white paste" (see p. 292). Light-foot studied the effect of various metals on the development of black by means of "basic" aniline hydrochloride and ammonium-chlorate, and he found vanadium superior to any other; the effect of this metal is almost miraculous, since according to Witz $\frac{1}{270000}$ of the weight of the aniline is sufficient to produce a good oxidation in a few days at 25°. In practice 0·0012 grm. of vanadium is used per litre of colour (about

* *Journ. Soc. Dyers and Col.*, 1890, p. 89.

$\frac{1}{10}$ grain or $\frac{1}{5000}$ oz. per gallon). The vanadium is used in the form of a chloride. (See p. 307.)

The addition of oxidisable substances, *e.g.*, glucose, to steam aniline-black colours has been recommended for the purpose of protecting the fibre against the strong oxidising action of the mixture. Adolf Lehne* has recently recommended the following process for dyeing aniline-black on cotton-yarn:—

Boil 400 grms. (4 lbs.) of wheaten starch with 5 litres (5 galls.) of water and allow to cool; add 60 grms. (6 lbs.) of sodium chlorate dissolved in

3 litres (3 galls.) of water,

100 grms. (1 lb.) of copper sulphide in paste (30 per cent.),

1200 grms. (12 lbs.) of aniline-salt dissolved in

2 litres (2 galls.) of water,

and pass the mixture through a fine sieve.

Give each hank two or three turns, wring out well and age for two days in moist air at 30° C.; the colour gradually passes from light green to black; after this pass for 10 minutes at 80° through a solution of 6 parts of bichromate and 5 parts of sulphuric acid in 10,000 parts of water; then work for 15 minutes at 80° in a bath consisting of 4 parts of soap in 1000 parts of water, to which 5 per cent. of glycerin (of the weight of the soap) has been added; finally rinse in water and dry at 30°. The black does not rub and the fibre is not appreciably weakened.

Few of the countless methods proposed for producing aniline-black have acquired practical importance. Many oxidising agents have been recommended but have not been generally adopted; manganese dioxide is the only one that need be mentioned here.

Aniline-black is sometimes topped with a weak solution of methyl-violet in order to render it ungreenable; the efficacy of this method depends upon the optical effect that when green is added to violet a blue shade is produced; hence the black simply becomes blue, and the greening effect is not manifested. The cotton being changed partially to oxycellulose by the oxidation process causes the methyl-violet (and other basic colours) to be fixed.

Aniline-black, when prepared by means of a chromate, always contains chromic oxide; therefore the colour can be topped with mordant colours which are dyed on chromic oxide—*e.g.*, with logwood. The topping makes the colour less prone to rub. The process of dyeing a light aniline-black and saddening with logwood, is used with advantage for the production of a very fast black, without incurring the risk of tendering the fibre. The advantages thus gained have induced A. Kertecz to recommend the following method:—At first aniline-black is produced; this is topped with diamine-black (Cassella), and the latter colour is diazotised on the fibre, and so fixed, by the process described on p. 446, as to become fast to washing.

* *Faerber Zeitung*, 1889-90, p. 332.

First Operation.—For 100 kgs. (lbs.) of cotton dissolve

7½ kgs. (7½ lbs.) potassium chlorate in
10 litres (1 gall.) water, and dissolve separately
13 kgs. 700 grms. (13¾ lbs.) aniline,
12 kgs. (12 lbs.) hydrochloric acid (32° Tw.) in water.

Mix the two solutions, and add cold—

30 grms. (½ oz.) copper sulphate in 1 litre (1 pint) water.

Dilute the mixture to 3° Tw.; pass the goods through this solution, wring, dry at 30° to 35°, and age; chroming at 80° follows as usual, or can be dispensed with; finally, the goods are soaped.

Second Operation.—Dye as usual with 3 per cent. of diamine-black RO (Cassella), with the addition of 5 per cent. of soda and 15 per cent. of Glaubersalt, diazotise and fix with phenylenediamine; a more bluish-black is obtained by developing with alphanaphthylamine instead of phenylenediamine; a still bluer by dyeing with diamine-black BO (Cassella). The diamine-blacks alone do not yield a full black; the aniline-black imparts fulness, brilliancy, and greater fastness to light.

Monnet's Aniline-Black.—Mm. Gilliard, P. Monnet et Cartier, of Lyons, have found that an ungreenable black can be produced with the aid of paraphenylenediamine, and have patented in Germany a process which is based on the use of this substance. They state that a mixture of equal molecules of paraphenylenediamine and aniline produces a brownish-black, whereas a mixture of 1 molecule of paraphenylenediamine with 2 or 3 molecules of aniline or toluidine yields good bluish-blacks, hence they mix the hydrochlorides of paraphenylenediamine in the corresponding proportions, and use for 100 kgs. (lbs.) of cotton, 4 to 6 kgs. (lbs.) of this mixture, 3 kgs. (lbs.) of sodium chlorate, and 40 grms. (about 1 oz.) of vanadium chloride; the bath is kept at 60° C., and thus a soluble dyestuff is formed. This is taken up by the fibre, and the bath becomes colourless.

Naphthylamine-Violet.—The bases of the aromatic series yield fast colours on oxidation by the aniline-black methods. These colours, however, have acquired but little importance. Alphanaphthylamine is used to a limited extent in calico-printing; but it imparts an objectionable smell to the goods, which can only be removed by laborious washing. It gives a dull greyish or brownish-violet, which is not quite so fast as aniline-black.

INDIGO (ARTIFICIAL).

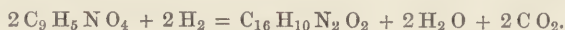


In 1880 Adolf Baeyer discovered after many years of study a method of preparing indigo from coal-tar, and also explained the chemical constitution of the compound. Both from a scientific and a practical point of view the second part of his discovery appears to be the more important, since, even at the present time, the practical

manufacture of indigo by his methods has not been realised, while all later experiments in this direction are based on his investigations and on his conclusions as to the chemical constitution of indigo.

At one time a process of blue-printing by means of orthonitropropiolic acid promised to be one of the fruits of his labours; but the inherent defects of this method and the introduction of Schlieper and Baum's excellent glucose process have checked its full development.

Orthonitrophenylpropionic Acid, $C_6H_4(NO_2)C\equiv C-CO_2H$ (shortly called *propiolic acid*), is converted by mild reducing agents (*e.g.*, glucose, milk sugar, and, notably, xanthogenate of sodium) into indigo:—

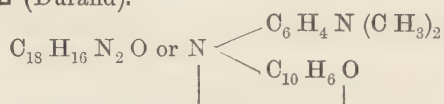


The indigo-blue produced by printing the "propiolic acid" together with xanthogenate is brighter than natural indigo and resists rubbing and soaping better. It combines well with oxidation colours—*e.g.*, aniline-black or cutch; but as the propiolic acid cannot be hot steamed the combination of the artificial blue with steam colours is precluded. The greatest drawback in the employment of propiolic acid is the disagreeable smell imparted to the fabric by the decomposition products of the xanthogenate (which is by far the best reducing agent for the purpose); hence the process has met with little favour, and, so far as we are aware, there is little demand for "propiolic acid."

K. Heumann* has recently discovered a new synthesis of indigo by melting phenylglycocoll with caustic alkalies and subsequent oxidising of the leuco-compound obtained.

B. Heymann has modified K. Heumann's reaction by heating phenylglycocoll with fuming sulphuric acid, and claims to have obtained in this way a high yield of *indigotine-disulphonic acid* or *artificial indigo-carmin*.

INDOPHENOL (Durand).



Indophenol, which has also been called *naphthol-blue*, is an *alpha-naphthoquinonodimethylanilineimide*. It is obtained by the action of nitrosodimethylaniline on alphanaphthol or by oxidising a mixture of para-amidodimethylaniline and alphanaphthol.

Indophenol possesses basic properties and dissolves in acids; it is, however, a very unstable compound in acid solutions and no permanent salts can be prepared. It is immediately decomposed by concentrated sulphuric acid, more slowly by diluted acids, into naphthoquinone and dimethylparaphenylenediamine. Reducing agents, both acid and basic, readily convert the indophenol into a leuco-compound, the indophenol-white (see below).

* *Journ. Soc. Dyers and Col.*, 1891, p. 8.

Indophenol is sold as a dark brown crystalline powder or as a dark blue paste with a bronze reflex. It is quite insoluble in pure or in alkaline water; but dissolves readily in alcohol, ether, or benzene, with a blue colour. Caustic alkalies have no action on the colour, diluted acids dissolve it with a yellow colour, the solution decomposes readily and yields on boiling the pungent smell of alphanaphthoquinone. Concentrated sulphuric acid dissolves it with a brownish-yellow colour; on diluting with water a brown precipitate is obtained.

Indophenol-White.— $C_{18}H_{18}N_2O$ or $N \begin{array}{l} \swarrow C_6H_4N(CH_3) \\ \searrow C_{10}H_6(OH)_2 \\ H \end{array}$

Indophenol-white, or *dimethylparaamidophenyl-oxalphanaphthylamine*, possesses both basic and acid properties, and is readily converted into indophenol by oxidising agents, such as bichromate, and even by atmospheric oxygen. It is prepared by reducing indophenol with stannous acetate (10° Tw.), and is sold by the manufacturers of indophenol as a yellowish-white paste for use in calico-printing in place of indigo. The commercial article is a compound with stannous oxide or stannous salt, which dissolves in boiling water and is not decomposed by acids; in alkaline solution it is readily converted into indophenol.

Application of Indophenol and Indophenol-White.—Indophenol resembles indigo in being readily reduced in alkaline solutions to a leuco-compound, which is soluble in the alkaline liquor. The attempts made to dye with indophenol alone by one of the vat-indigo methods were not successful, because the fibre did not readily absorb the leuco-compound. Much better results are obtained if indophenol is mixed with indigo in the ratio of 1:3. Indophenol is now used in this form in increasing quantities (indigo-indophenol-vat). O. N. Witt* has brought forward the hypothesis that when indophenol-white alone is in solution it forms a very intimate compound with alkali which is not readily dissociated by the fibre; but when indigo-white is also present the indophenol-white combines with this substance and is more easily taken up by the fibre; and that then oxidation causes the compound to be resolved into indophenol and indigo, which are separately deposited.

Indophenol in combination with indigo is used for the dyeing of cotton, wool, and union goods by the following method, which has been worked out by H. Koechlin, G. Galland, and the makers of indophenol.

1. *Stock Vat.*—In a 100 gallon cask (500 litres) mix—

120 litres (24 galls.) cold water,
6 kgs. 750 grms. (14 lbs.) zinc dust, previously mixed to a paste with
30 litres (6 galls.) water; then add, continuously stirring,
36 litres ($7\frac{1}{4}$ galls.) sodium bisulphite (55° Tw.); or 26 litres ($5\frac{1}{4}$ galls.)
sodium bisulphite (75° Tw.).

* *Faerber Zeitung*, 1889-1890, p. 2.

Stir well for 15 minutes, taking care that the temperature does not rise above 35°, and then add

16 to 18 litres (3½ to 3¾ galls.) caustic soda (71° Tw., and containing about 32 per cent. Na O H).

For *cotton- or woollen-yarns* and for *unions* the following quantity of caustic alkali is recommended:—

6 litres (1¼ galls.) caustic soda (71° Tw.), and
7 to 8 kgs. (14 to 16 lbs.) quicklime, previously slaked with
30 litres (6 galls.) water.

And for *slubbing*—

3 litres (5 pints) caustic soda (71° Tw.), and
10 litres (2 galls.) ammonia (20 per cent. N H₃).

Stir continuously after the alkali has been added, and while the temperature is rising add the following mixture (previously ground as usual for indigo)—

7½ kgs. (15 lbs.) indigotin, or 10 kgs. (20 lbs.) best indigo,
3½ kgs. (6 lbs. 10 ozs.) indophenol,
2 litres (3¼ pints) caustic soda (71° Tw.),
30 to 35 litres (6 to 7 galls.) water.

Make up to 500 litres (100 galls.) by adding cold water or, better, exhausted vat-liquor, stir from time to time, cover the cask, and allow to stand for 24 to 48 hours, until the reduction is complete and the vat-liquor shows a canary-yellow colour; if this colour has not appeared within 48 hours, add some hydrosulphite liquor to complete the reduction.

2. *Hydrosulphite Liquor*.—Mix in a wooden cask

2 kgs. (4 lbs.) zinc-dust with
30 litres (6 galls.) water, and add, while stirring continuously,
17½ litres (3½ galls.) sodium bisulphite (55° Tw.), or
12½ litres (2½ galls.) sodium bisulphite (75° Tw.).

Stir 15 minutes longer, taking care that the temperature does not rise above 30°, and then add

4 litres (7 pints) caustic soda (71° Tw.).

For *cotton- or woollen-yarns* and for *unions* the quantity of caustic alkali should be—

2 litres (3½ pints) caustic soda (71° Tw.),
1½ to 2 kgs. (3 to 4 lbs.) quicklime, slaked with
10 litres (2 galls.) water.

For *slubbing* the quantity required is—

500 to 750 cc. (2 to 3 pints) caustic soda (71° Tw.), and
1 litre (3½ pints) ammonia (20 per cent. N H₃).

Fill up with cold water to 60 litres (12 galls.), allow to settle, and use the clear liquor (in case a clear vat is required; but, if not, stir up before using). The hydrosulphite liquor must be distinctly alkaline, and caustic soda, milk of lime, or ammonia should be added, if necessary, to make it so.

3. *Dye-Vat*.—Fill the vat three-quarters full with water, and add, first, a small amount of hydrosulphite liquor (in order to prevent any oxidising action by the air dissolved in the water); and then add the

required quantity of liquor from the stock-vat and dye, exactly as in an indigo-vat—cotton at the ordinary temperature, wool and union goods at 40°.

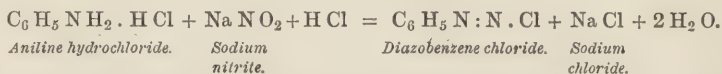
After the dyeing allow the goods to oxidise in the air; passing of the goods through potassium bichromate (2 parts in 1000 of water) facilitates the oxidation, but it is not essential. Finally, wash the goods in water, to which a very small amount of hydrochloric acid may be added if lime has been used. The colour from the wash water can be recovered and used again for preparing stock-vat liquor.

The vat is kept up to the required strength by fresh liquor from the stock-vat; when it becomes greenish some hydrosulphite liquor is added until it regains its normal canary-yellow colour. If the clear liquor only is used from the stock-vat, the indophenol-white can be extracted from the sediment with water containing some hydrosulphite liquor; the extract may be used for preparing a fresh stock-vat.

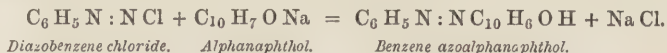
Indophenol in combination with indigo is, without doubt, a very good substitute for indigo. The colour is nearly as fast to light as indigo; fast to alkalies, and rubs less than indigo. Indophenol deserves also to be called fast to milling, although it is asserted that the tone is slightly altered thereby. The saving in dyeing with indophenol and indigo in the above proportion is considerable, and has been estimated at from 11 to 25 per cent. for cotton goods.

INSOLUBLE AZO-COLOURS, DEVELOPED IN THE FIBRE.—

The primary amines of the aromatic series are converted by nitrous acid and by nitrites in acid solution into diazo-compounds, for instance:—



The diazo-compounds combine with phenols in alkaline solutions (and, under suitable conditions, with aromatic amines) to form azo-compounds:—



The mode of manufacture of the azo-colours is in accordance with these equations. The azo-compounds which do not contain sulphonic acid groups are insoluble in water, and many of these, notably those produced from betanaphthol, are insoluble in caustic soda. The ordinary acid colours, *i.e.*, the sulphonated substances, are soluble in water, and cannot be fixed satisfactorily on the vegetable fibres; the non-sulphonated compounds, when once prepared, cannot be dyed on account of their insolubility. It is, however, possible to produce the latter in the fibre, and thus to obtain insoluble colours which resist washing fairly well. The mode of procedure in dyeing is first to impregnate

the fibre with the phenolic solution, and then to pass it through the solution of the diazo-compound; the colour is developed in the second bath.

The insoluble azo-colours are very similar to their sulphonic acids, the acid azo-colours. They possess the same chromophorous and auxochromous groups and dye similar shades. Their tinctorial power is greater, but their resistance to light is less than that of the acid colours.

The *phenols* contain a hydroxyl group, and are—by virtue of their constitution—soluble in caustic potash and soda, less readily in ammonia, and not soluble in alkaline carbonates; they are precipitated from the alkaline solutions by the weakest acids, even by carbon dioxide. (See pp. 316 and 317).

The *diazo-compounds* are unstable substances. In the solid state they are explosive; they are, however, never prepared in this form for dyeing purposes. The aqueous solutions decompose gradually, but more rapidly in proportion as the temperature is higher, thereby forming resinous substances from which no pure products can be obtained. Hence it is essential to keep the temperature low, if possible below 5° C. The diazo-compounds decompose rapidly in alkaline, but are less liable to change in strong mineral acid solutions; hence they are prepared with an excess of acid, and the solutions are kept acid. The successful preparation of azo-compounds of all kinds mainly depends on the purity of the diazo-compounds.

The diazo-compounds do not combine with the phenols in the presence of strong mineral acids. In manufacturing azo-colours on the large scale (away from the fibres) the diazo-solution is run in a thin stream into the alkaline solution of the phenol. The mineral acid of the former is saturated by the alkali of the latter, and the formation of the azo-colour takes place before the diazo-compound has decomposed. In dyeing, this process is not applicable, since it is impossible to charge the phenol in the fibre with enough alkali to neutralise the acid. The Hoechst Farbwerke have introduced an important modification of this process, which was first worked out by G. Galland. It is based on the fact that acetic acid does not strongly retard the process of combination; in this method sufficient sodium acetate is added to the diazo-compound to convert the free mineral acid into the sodium salt, and to liberate the acetic acid, which becomes more or less saturated by the excess of alkali used with the phenol.

Application.—The insoluble azo-colours are almost exclusively produced on the cotton fibre. Linen and the other fibres can also be dyed with them, but, so far as is known, they have not been practically applied to wool and silk.

The insoluble azo-colours (especially those obtained from betanaphthol) are very fast to washing, acids, and alkalies; they do not bleed at all, but are liable to rub, especially if not properly prepared.

The fastness to light is not great, as a rule; but apparently it can be improved by treatment with a boiling solution of copper sulphate (see below). Some of the colours are volatile, and slowly escape from the fibre; but those which are obtained from betanaphthol are free, or almost free, from this defect, and are, moreover, quite insoluble in caustic alkalies; whereas the compounds from alphanaphthol and other phenols are soluble. The betanaphthol colours are chiefly used both for their superior fastness and for the brightness of their shades.

The following colours are obtained with the bases chiefly used in combination with alpha- or betanaphthol:—

Name of the Base.	Colour of the Combination with Betanaphthol.	Colour of the Combination with Alphanaphthol.
1. Aniline,	Orange-yellow.	Cutch-brown.
2. Paratoluidine, . .	Yellowish-orange.	Do.
3. Metanitriline, . .	Fiery reddish-yellow.	Brownish-orange.
4. Paranitriline, . .	Orange-red.	Do.
5. Nitroparatoluidine, .	Orange.	Very fine cutch-brown.
6. Alphanaphthylamine, .	Bluish claret-red.	Reddish puce.
7. Betanaphthylamine, .	Turkey-red.	Do.
8. Amidoazobenzene, . .	Red.	Do.
9. Orthoamidoazotoluene, .	Yellowish claret-red.	Do.
10. Benzidine,	Puce.	Dark brown.
11. Tolidine,	Puce.	Do.
12. Orthonitroparaphenitidine,	Bright red.	...

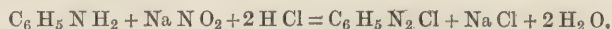
The production of the insoluble azo-colours in the fibres is effected in three stages:—

- (1) Diazotisation of the base;
- (2) Impregnation of the fibre with the phenol;
- (3) Developing of the colour.

It is essential that the proper quantities of the various substances be used, as otherwise no useful colour or no colour at all is obtained; the dyeing of these colours requires the greatest exactness.

The diazo-compound must be kept at a temperature not exceeding +5° C. by means of large lumps of ice floating in the solution. It is not advisable to save the expense for ice. This material is certainly cheaper than the steam used in the usual dyeing processes.

(1) *Diazotising*.—One equivalent of the base requires one equivalent of sodium nitrite and two equivalents of acid for complete diazotisation, according to the equation:—



Since, however, the diazotisation proceeds better, and the diazo-compound is more stable in the presence of an excess of acid, about three equivalents of acid are used.

The equivalents of the bases are given below:—

Aniline, 93.
 Toluidine, 107.
 Xylidine, 121.
 Cumidine, 135.
 Anisidine, 123.
 Phenitidine, 137.
 Naphthylamine, 143.

Nitraniline, 138.
 Nitrotoluidine, 152.
 Amidoazobenzene, 197.
 Amidoazotoluene, 225.
 Benzidine, 92.*
 Tolidine, 106.*

The equivalent of hydrochloric acid gas (HCl) is 36.5. The commercial products, however, contain but 28 per cent. (for 28° Tw.) or 32 per cent. (for 32° Tw.) of HCl; the equivalent of hydrochloric acid, 28° Tw., is 130, and that of acid, 32° Tw., is 114. The hydrochloric acid referred to below will be that which has the strength 28° Tw., the equivalent of which is 130. The equivalent of sodium nitrite is 69; but as the commercial article contains impurities, and as a small excess of the nitrite is required, the equivalent 75 is more suitable; 150 grms. of sodium nitrite are dissolved in water, and the solution is diluted to 1 litre, so that it has double the standard strength. In the following data it is this solution of 150 grms. of nitrite per litre that is referred to.

Diazotisation of Aniline.—93 grms. of aniline are mixed with 390 grms. of hydrochloric acid (28° Tw.) and 200 cc. of water; the solution is cooled by throwing ice directly into the liquor; 500 cc. of the nitrite solution are added gradually while stirring continuously; the temperature must not rise beyond 5°. When all the nitrite has been added, iodide-starch paper must be turned blue *instantaneously* by a drop of the solution through liberation of iodine;† should it not change, either more nitrite or more acid must be added. To ensure accuracy, *this test should be made every time*. A small excess of nitrite is not injurious; but care should be taken to avoid the evolution of a very strong smell of nitrous acid or of red vapours from the diazo-solution.

The diazo-solution is filtered after 15 minutes' standing and the filtrate is diluted to 10 litres. A short time before using the diazo-solution add 300 grms. of sodium acetate in order to neutralise the mineral acid.

The bases named in the first column of the foregoing list are diazotised exactly in the same way, except that instead of 93 grms., the number of grms. expressed by their equivalents are used; for example, 107 grms. of toluidine or 143 grms. of alpha- or beta-naphthylamine or

* Benzidine and tolidine are diamines, since they contain the amido-group NH_2 twice in their molecule; hence their equivalents are only one-half of the molecular weights, the latter being 184 and 212 respectively. The metrical system of weights and measures will be used in the sequel. They can readily be converted into the English system when required.

† The iodide-starch paper is prepared by dissolving a few grammes of iodide of potassium in 1 litre of thin starch paste, saturating filter paper in this solution, and drying in pure air. It is advisable to keep this paper in a well closed glass. Iodide-starch paper which has been kept too long shows the iodine reaction even in the absence of free iodine.

92 grms. of benzidine. The naphthylamines, however, must be brought into a suitable form, before they can be diazotised.

Melt 143 grms. of *alphanaphthylamine* in 2 litres of hot water, add 200 grms. of hydrochloric acid (28° Tw.) and heat the mixture on the water bath, until all is dissolved; then add 190 grms. of hydrochloric acid and stir until quite cold. Into the well cooled liquor pour 550 cc. of the nitrite solution, introducing it below the surface, and stir well; the temperature should not rise above + 3° C. After 15 minutes' standing, filter, and dilute the filtrate to 10 litres; add 300 grms. of sodium acetate a short time before using.

Dissolve 143 grms. of *betanaphthylamine* on the water-bath in 130 grms. of hydrochloric acid (28° Tw.) and 2 litres of water, filter the hot solution and stir rapidly until quite cold. To the resulting greyish-white paste add 260 grms. of hydrochloric acid and sufficient ice; and then 550 cc. of the nitrite solution; the temperature should not rise beyond + 3°. After 15 minutes' standing, filter, make up to 10 litres, and add 300 grms. of sodium acetate before using.

The bases named in the second column of the same list may be treated in the same way. Their hydrochlorides, however, are sparingly soluble in water and they are not readily diazotised. The Farbwerke Hoechst have prepared mixtures of these bases with the required amount of nitrite, which are designated with the letter N (= nitrite); for instance, amidoazobenzene N. These mixtures are readily diazotised on being added to water containing the necessary quantity of acid. Instructions for use are given for these (patented) preparations; the required quantities of acid, &c., can also be calculated from the above data.

(2) *Impregnating*.—The naphthols only have been practically applied, but the other phenols may be used in a similar way.

Stock Solution for Cotton Yarn.—1,440 grms. of alpha- or beta-naphthol (previously broken up into small lumps) are dissolved in sufficient caustic soda (400 grms. of pure caustic soda or correspondingly more of the weaker commercial articles) and 2 to 5 litres of hot water. An excess of alkali is not injurious. When the naphthol has dissolved, the liquor is diluted to 10 litres. We shall call this diluted liquid "stock liquor." 1 litre of stock liquor is diluted with 5 to 10 litres of water and 400 grms. of soda ash are added. For brightening the colours stannate of soda, Turkey-red oil, and other alkaline or neutral substances may be added to this solution. The addition of oil to the naphthol bath is claimed as an invention by R. Holliday (Brit. patent, 1889, No. 20,064).

Cotton hanks are impregnated with the naphthol solution in lots of 1 kilogramme each, and after each lot 50 cc. of stock liquor and 20 grms. of soda ash are added to the bath to restore the strength.

It is essential that the material be impregnated very evenly; hence it is best to treat hanks in a tramping machine which does both the steeping and the wringing. The depth of the ultimate colour depends

chiefly on the quantity of naphthol which has been taken up by the fibre in this operation. Hence, stronger or weaker solutions may be used; but the strength must be preserved uniform to obtain equal shades.

Loose cotton and *cotton yarn* may also be treated in large lots in hydro-extractors provided with a draw-off tap. Other mechanical dyeing machines can be used equally well.

Cotton piece goods are treated on the jigger. The padding liquor may be prepared as before, but less diluted. Since, however, in this case a strong causticity of the liquor is less objectionable to the workmen, it may be prepared by dissolving 1,440 grms. of naphthol in 5 litres of hot water containing 800 grms. of caustic soda (100 per cent. NaOH), and diluting to 100 litres. The fabric is padded with this solution.

Good results are obtained by drying the impregnated material; it must be dried, however, quickly, otherwise it becomes brownish, and the colours are not satisfactory. It should be worked up soon.

(3) *Developing*.—The impregnated material is worked a few times in the diazo-solution, prepared as stated above, and then thoroughly washed in water. To prevent rubbing it must be soaped at 60°, and washed again in water. The diazo-solution may be used continuously; it should be thrown out, however, if it begins to decompose rapidly. A good colour is obtained by using the exact proportions of base, acid, nitrite, acetate, naphthol, and alkali, and working carefully. The production of these colours requires, however, unusual exactness, and cannot be effected by an ordinary workman without the help of an educated dyer.

The colours can be improved in fastness by treatment with a boiling solution of copper sulphate, or with ammonio-cupric solutions at 40° to 50°. The shades are thereby more or less altered. (See pp. 436 and 450.)

H. Koechlin * has described several colours which he has prepared on piece goods.

The cotton pieces are first padded with a solution of 25 parts of beta-naphthol in 25 parts of caustic soda, 100° Tw. (46 per cent. NaOH), and 100 parts of water. After drying, the prepared goods are passed for half a minute through a diazotising bath. A bath for blue is prepared with 100 parts of safranine dissolved in 75 parts of hydrochloric acid and 1,000 parts of water, and, further, with 20 parts of nitrite, 125 parts of water, and 250 of ice, to which are added, lastly, 250 parts of acetate and 1,000 parts of water. The blue is not very fine, and not fast to light.†

Kalle & Co.‡ have recently taken out a patent in Germany for producing yellow to brown colours on cotton by first mordanting with tannin, catechu, &c., and then passing through a diazo-solution.

* *Journ. Soc. Dyers and Col.*, 1890, p. 152.

† A blue may also be produced, according to Fischesser & Pokorny (*Journ. Soc. Dyers and Col.*, 1892, p. 42), by padding first in an alkaline solution of beta-oxynaphthoic acid, m.p. 216°, and developing in diazotised dianisidine.

‡ Germ. Patent, 55,837; *Journ. Soc. Dyers and Col.*, 1891, p. 147.

CACHOU DE LAVAL.* CATTU ITALIANO.

(Poirrier).

(Lepetit and Dollfuss).

This colouring matter, which was discovered in 1873 by Croissant and Bretonnière, takes a unique place amongst the dyestuffs by virtue of its origin and probably also on account of its constitution. Very little is known about its composition, except that it is an organic compound which contains sulphur as an essential constituent. It is produced by melting organic substances, such as sawdust, turf, bran, leaves, and other cellulose matter, with sodium sulphide.

Cachou de Laval behaves like a reduced colouring matter, the bath forming a kind of vat which in a certain sense resembles reduced indigo. The solutions are intensely dark green, and this colour is also shown by the cotton during the dyeing; but on exposure to the air it rapidly turns into a brownish-grey, the colouring matter becoming insoluble and remaining in this form in the fibre. If solutions of the dyestuff are exposed to the air for some time, they also gradually turn into a brownish-grey, while sulphur and a part of the colouring matter are separated. Cotton when dyed in such a solution assumes a brown shade; but the colour is almost entirely removed by washing; hence solutions of cachou de Laval must be prepared each time before dyeing and not be kept for further use. It is, moreover, of importance to keep the colouring matter in well closed boxes, protected from moisture, as it greedily absorbs water and air, thus becoming insoluble by oxidation.

If acids are added to cachou de Laval, sulphuretted hydrogen is developed and the colouring matter is separated as a completely insoluble precipitate, together with sulphur. With metallic salts cachou de Laval forms mostly grey or dark brown precipitates. These properties make it possible to fix the colouring matter after dyeing, especially by means of certain acids or metallic salts, such as nitric acid, bichromate, or permanganate of potash, nitrate of iron, &c., which have simultaneously an oxidising effect. The shades with the various mordants do not show great variety; dilute nitric acid furnishes a brighter tone with a yellowish tinge; bichromate acts similarly, the colour becoming lighter, especially on heating; copper sulphate produces a slightly grey colour; and permanganate a fine brown (by the separation of manganese dioxide).

Application.—Cachou de Laval is dyed on unmordanted cotton, and is especially adapted as a bottom for many mode colours. It is not suitable for dyeing animal fibres. The colouring matter requires soft water; hard water is to be purified by heating with soda. The dyestuff is dissolved in hot—not boiling—water and the solution filtered through a sieve. The bath should be kept as strong as possible, and a relatively large amount of colour is required (1 to 10 parts per 100 parts of dye liquor); Glaubersalt may be added—40 to 70 per cent. of the weight of the dyestuff—to exhaust the dye-liquor better. The cotton

* E. Lepetit, *Journ. Soc. Dyers and Col.*, 1890, p. 110.

material is previously boiled with or without soda, then entered into the bath at 30° and turned rather rapidly at first; the temperature is raised within an hour and a quarter to 72° or 78°; the goods are lifted, 10 per cent. of common salt is added to the bath, and, after a good stirring, they are manipulated for another quarter to half an hour, until the bath is exhausted—that is, till the greenish colour has changed into brown; then follows good rinsing and drying. The colours become faster if the goods are passed through dilute acids, such as sulphuric, hydrochloric, or nitric acids, or solutions of certain salts, *e.g.*, potassium bichromate, copper sulphate, potassium permanganate, ferrous or ferric sulphate. This property allows of cachou de Laval being combined with mordant colours. It is optional to top the cachou bottom with natural colouring matters and mordants, as well as with artificial dye-stuffs, or to add logwood, fustic, quercitron extract or ordinary cutch to the cachou de Laval in the first bath, and afterwards to pass the material through metallic mordants. Cachou de Laval, like the direct cotton colours, acts as a mordant for basic colours; but the shades thus obtained have little fastness to soap. If colours fast to washing are required, the preference is given to the direct cotton colours.

Cachou de Laval produces grey to buff-brown shades, which stand light fairly well, and are exceedingly fast to soap; boiling soda (1½° to 3° Tw.), cold solutions of chloride of lime (1½° Tw.), and acids have very little action on it. Alkaline solutions of hydrogen peroxide cause a rapid decolorisation of the shade.

CANARIN or PSEUDOSULPHOCYANOGEN. $C_3N_3S_3H$.

This substance is obtained by the oxidation of potassium thiocyanate by means of chlorine, nitric acid, or a mixture of potassium chlorate with sulphuric or hydrochloric acid.

Canarin is a yellow amorphous powder, which is insoluble in water and in alcohol, but soluble in a 10 per cent. boiling solution of borax. It also dissolves without decomposition in concentrated sulphuric acid or dilute caustic potash lye; but when boiled continuously with caustic potash it is decomposed with the formation of potassium thiocyanate.

Application.—Canarin is used in cotton dyeing. It yields yellow and orange shades, which are distinguished by fastness to light, acids, alkalies, and chlorine. It can also be used as a mordant for the basic colours, and is suitable for the production of compound shades in conjunction with the latter.

The dye-bath is prepared with a solution of canarin in borax, and a small quantity of soap is added. The cotton is introduced into the cold bath, and the temperature gradually raised to the boil. Finally the material is rinsed in water and dried.

Calcareous water must be avoided or purified in dyeing with canarin.

Canarin can also be produced in the fibre by the oxidation of thiocyanates.*

* Schmidt, S. Dreyfuss, *Journ. Soc. Dyers and Col.*, 1887, p. 24.

PART VIII.

MINERAL COLOURS.

THE mineral colours have lost much of their former importance since the discovery of the aniline colours. Still they are produced in considerable quantities on account of their fastness and the low cost of their production. The mineral colours are totally different from the natural and artificial organic colouring matters both in their general chemical characters and in their tinctorial properties and methods of application.

The mineral colours which are now used to any considerable extent in dyeing are the following :—

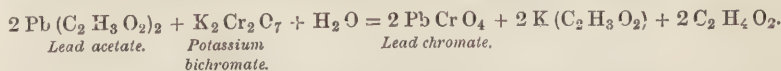
- | | |
|-------------------|---------------------------------|
| 1. Chrome-yellow. | 4. Manganese-brown. |
| 2. Chrome-orange. | 5. Iron-buff and nankin-yellow. |
| 3. Chrome-green. | 6. Prussian blue. |

Numerous mineral substances, however, are used as pigments in calico-printing.

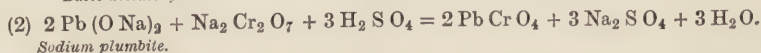
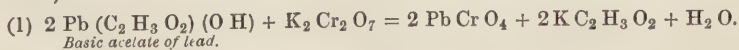
We shall here describe only those colours which are still important for the dyeing proper of the textile fibres.

CHROME-YELLOW or CHROMATE OF LEAD, Pb Cr O_4 .

Chromate of lead occurs native, and is manufactured in large quantities as a pigment by precipitating the solution of a lead salt (acetate or nitrate of lead) with bichromate of potassium or sodium :



The compound can also be produced from a basic lead salt or from an alkaline plumbite (compound of lead hydroxide and an alkali) (see p. 296).



Chrome-yellow forms an orange-yellow powder, and is quite insoluble in water and other neutral solvents, but dissolves readily in nitric acid

and in caustic potash or soda; the latter agents, however, convert it first into a basic lead chromate. (See *Chrome-orange*.)

Chromate of lead is used as an oxidising agent in the laboratory, and has also been recommended as such for the production of aniline-black by oxidising the aniline in the fibre.

Chrome-yellow is produced in dyeing by first impregnating the fibre with a lead salt, and then passing the material through a solution of a bichromate. The processes are precisely similar to those which occur in mordanting and dyeing with the mordant colours; the lead salt plays the rôle of the mordant and the bichromate acts as the dyestuff. The analogy goes still further, inasmuch as the dyestuff possesses a distinct chromophor "Cr," and—in the form of free chromic acid, H_2CrO_4 —the auxochromous group (OH). Finally, lead is not the only mordant for the bichromate dyestuff, although by far the best, since soluble barium salts produce a similar chrome-yellow.

Application.—Chrome-yellow is dyed on cotton only. The colour varies from a light lemon-yellow to a full orange-yellow, and is distinguished by almost absolute fastness to light, soap, and acids; by alkalies it is turned orange (see below); by sulphuretted hydrogen it becomes brownish, lead sulphide being formed. To produce the colour the cotton is impregnated with nitrate or acetate of lead, and after precipitation of the lead in the fibre, as oxide or sulphate (by means of ammonia, lime, or sodium sulphate), is passed through a dilute solution of potassium bichromate. Another method is to impregnate the material with a plumbite and then to pass it through an acidulated solution of bichromate.

First Method.—A basic salt is used in order to save the expense of acid as also to precipitate more lead in the fibre.

Preparing of Stock Liquor.—Dissolve, boiling, 100 kgs. (100 lbs.) of brown sugar of lead and 50 kgs. (50 lbs.) of litharge in 360 litres (16 galls.) of water and allow to settle; the liquor should stand at 125° Tw.

Dyeing.—Pass the yarn through lime water (1½° Tw.) and wring; then work in a solution of basic lead salt prepared by diluting stock liquor with cold water to 10° Tw., wring out and pass through another tub with lime water (1½° Tw.). The lead liquor is used continuously and maintained at the same strength by the addition of fresh stock liquor. The chrome-bath is prepared with about 6 grms. of bichromate of soda per litre (6 lbs. for 100 galls.)—dissolved in water—and from time to time freshened up with fresh bichromate solution. The yarn is passed through the chrome-bath and then turned a few times in water (containing 1 part of hydrochloric acid for 300 parts of water), finally washed in water and dried.

Second Method (Lemon-Yellow).—Prepare a stock liquor by dissolving 100 kgs. (100 lbs.) of brown sugar of lead in 800 litres (80 galls.) of water to stand at about 16° Tw. Fill a vat holding 200 litres

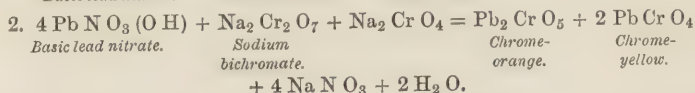
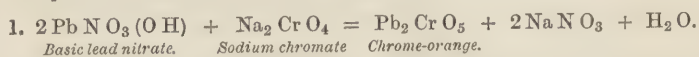
(40 galls.) with water and add $1\frac{1}{2}$ litres (3 pints) of stock liquor and 5 litres (1 gall.) of caustic soda lye (71° Tw. = 32 per cent. NaOH), turn the yarn about three times in the bath, wring and pass through the chrome-bath, wring, wash, and dry. The chrome-bath is prepared for a vat of 200 litres (40 galls.) with $1\frac{1}{2}$ kgs. (3 lbs.) of bichromate of soda and 200 grms. (6 oz.) of sulphate of zinc. Both vats are used continuously, and are regularly freshened up; for restoring the strength of the chrome-liquor a solution may be kept of 10 parts of chromate and $1\frac{1}{2}$ parts of sulphate of zinc in a sufficiency of water.

The depth of the ultimate shade obtained by either method is mainly dependent on the strength of the lead solution, and on the quantity of lead oxide which is deposited in the fibre.

The yarn is very heavily weighted by the dyeing with chrome-yellow—even more than 40 per cent.—and to this fact the extensive use of chrome-yellow at the present time is due. Chrome-yellow must be considered to be a poisonous dyestuff, as it cannot be denied that the dust of the colour which is rubbed from the materials is injurious to the health of the work-people who handle the dry yarn (as in weaving, &c.). Various other dyestuffs of easier application are now in the market which might advantageously replace chrome-yellow; for instance, the yellows of the direct cotton colours.

CHROME-ORANGE.

Chrome-orange consists of a mixture of normal lead chromate (chrome-yellow) and basic lead chromate, Pb_2CrO_5 . It is also used as a pigment. It is produced by precipitating the solution of a basic lead salt with sodium bichromate or chromate; the colour appears the redder the more alkaline the mixture is—i.e., the less chrome-yellow the ultimate colour contains.



Chrome-yellow may be converted into chrome-orange by the action of alkalies or lime water; it is in this way that chrome-orange is produced in dyeing.

Chrome-orange forms an orange to red powder; it resembles chrome-yellow in its chemical properties.

Application.—Chrome-orange is produced in dyeing, as stated above, by the action of alkalies on chrome-yellow which has been previously fixed on the fibre by any of the usual methods. For this purpose the yarn is dyed with chrome-yellow, washed in water, and then passed through boiling clear lime-water; the cotton must be removed from the lime-water bath as soon as the full orange colour

is developed, otherwise the colour loses brilliancy; after this the material is washed and dried.

A *three-dip orange* is produced by the first method for chrome-yellow, but in the following order:—(1) Lime-bath, (2) lead-bath, (3) lime-bath, (4) lead-bath, (5) chrome-bath, (6) lead-bath, (7) chrome-bath, and, finally, (8) boiling lime-bath for “raising” the orange.

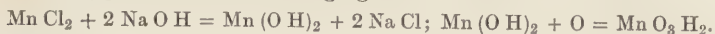
Chrome-orange is a full red-orange colour which equals chrome-yellow in fastness, except that it is fast to alkalis, but is affected by acids.

CHROME-GREEN.

Chrome-green consists chiefly of chromium hydroxide, which has been described in the chapter on mordants (p. 241, &c.). The hydroxide yields a very light shade of sea-green, hardly visible in artificial light, and rarely used now. In former years a *chromium arsenite* was produced on the fibre by mordanting with a chromium salt, and then passing through a hot solution of arsenic (arsenite of soda). This process yields a moderately full and very fast green, which does not appear very different when seen by daylight or by artificial light; but its poisonous character renders its use objectionable. Phosphate and silicate of soda have similar effects, but give inferior results. Chromium oxide can be produced on cotton by the usual mordanting methods, and on wool by saturating the fibre with a hot or cold strong solution of bichromate, and then passing the material through sodium bisulphite; by repeating the processes fuller colours are obtained. The colour known on cotton as “kaki” appears to be produced by precipitating on the fibre a mixture of chromic and ferric hydrates.

MANGANESE-BROWN or MANGANESE-BRONZE (BISTRE).

Manganese-brown has been mentioned in the description of the compounds of manganese (p. 299). It is a hydrate of manganese peroxide, and is produced by precipitating manganous hydroxide in the fibre, and then oxidising this compound with the aid of the atmospheric oxygen or such oxidising agents as chloride of lime:—



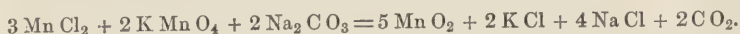
Manganese-brown is probably a hydrate of the peroxide, Mn O_2 , but containing less water than the compound, $\text{Mn O}_2 \text{ H}_2$.

Application.—Manganese-brown is dyed on the cotton fibre, and produces a full neutral brown, which is almost absolutely fast to light, soap, dilute acids, and alkalis. For the production of the colour the solution of manganous chloride, obtained as a bye-product in the manufacture of chloride of lime and known as “bronze liquor,” is used, after neutralising any free mineral acid which may be present. The cotton is impregnated with the manganous liquor, and then passed through a hot solution of caustic soda (2-3° Tw.). It is important that the caustic soda should be free from carbonic acid, because that impurity causes manganous carbonate to be precipitated in the fibre, which does not

oxidise readily, and is liable to produce an irregular colour; nor should the alkaline liquor be too cold or too dilute, otherwise a manganous hydrate is formed which also does not readily oxidise. The hydrate is at first colourless, but it soon oxidises and becomes brownish. The oxidation by the air, however, is not sufficient to produce a full brown, and a passage through a weak solution of chloride of lime or through a bichromate-solution is required to complete the oxidation.

The process is simplified by adding the chloride of lime directly to the solution of caustic soda; in this case precipitation and oxidation take place simultaneously.

J. Depierre* has recently proposed a new method whereby potassium permanganate is utilised both as an oxidising and as a colouring agent. The material is padded in a solution of manganous chloride containing 400 grms. (4 lbs.) of the salt per litre (gallon) of water, dried in the hot flue, and then passed at 45° through a bath which contains 100 grms. (10 lbs.) of potassium permanganate and 60 grms. (6 lbs.) of soda-ash per litre (10 galls.) The brown is formed according to the equation—

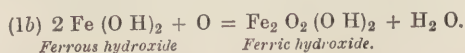
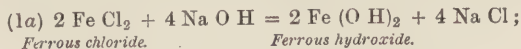


Endler has produced a brown colour on cotton piece goods by padding them with a solution of manganous chloride, and, after rapidly drying, passing them through a solution of potassium bichromate neutralised with ammonia. A similar steam colour was produced by Balanche. The products have been objects of repeated investigations, and contain probably, in addition to hydrated oxides of manganese, chromic oxide, and chromates.† The manganese-brown may be employed as an oxidising agent for the production of aniline-black and allied colours; for this purpose the cotton, after having been dyed brown, is impregnated with the aniline salt.

IRON-BUFF and NANKIN-YELLOW.

These two colours, which differ only by the depth of the shade, consist of hydrated ferric oxide, and they resemble certain kinds of ochre; most of the similar pigment colours, however, consist of anhydrous ferric oxide.

Iron-buff and nankin-yellow are produced by precipitating a ferrous or ferric salt with an alkali or alkaline carbonate; in the case of a ferrous salt being used, the resulting oxide is oxidised subsequently by the air or by such oxidising agents as chloride of lime.



* *Journ. Soc. Dyers and Col.*, 1891, p. 26.

† *Ibid.*, 1888, p. 46.

Application.—The Iron-buffs are dyed chiefly on cotton; they yield from yellow to light brown colours, which are fast to light, soap, and alkalis, but are sensitive to the action of acids.

The colours can be produced by the methods which are employed for the fixation of iron mordants on cotton (see p. 275).

Pyrolignite of iron, however, cannot be employed for this purpose, because it contains too much tarry matter, and does not produce pure shades; pure acetate of iron can be used. Nor can the iron compound be fixed by means of cow- or sheep-dung, since it would attract animal or vegetable colouring matter, which would dull the shade; the ordinary mineral fixing salts, such as silicate, phosphate or, arsenate of soda, are used.

For the oxidation of the ferrous salts or hydroxide a passage through solution of chloride of lime is of advantage. Concentrated ferrous solutions have a weakening influence on the cotton fibre, especially if the oxidation proceeds rapidly, and this fact must not be lost sight of. If a highly diluted solution of a ferric salt is used, some glycerin should be added, in order to prevent a dissociation of the salt.

The dyeing process can be repeated for the production of fuller shades.

PRUSSIAN BLUE.

The chemical properties of Prussian blue have been described in a previous chapter (p. 274). Prussian blue, strictly speaking, is not a mineral colour, since the prussiates, its chief constituents, are organic compounds; the colour consists, however, largely of iron, and is so similar to the metallic compounds that we follow the general custom by describing it among the mineral colours.

Prussian blue may be considered to be a mordant colour produced by the dyestuff "yellow prussiate," and by the ferric mordant; the colour deserves to be called polygenetic, since the prussiates produce various coloured products with most of the metallic oxides; Prussian blue, however, is the only colour which is used in dyeing, printing, or painting.

Application.—Prussian blue is produced on the textile fibres by two essentially different methods. The first is to mordant with ferric oxide and to dye with yellow prussiate; it is used for the dyeing of cotton and silk. The second method is based on the decomposition the prussiates undergo with formation of Prussian blue when they are heated in acid solutions; this process is used in woollen dyeing and in textile printing.

Frequently a stannous salt is added either to the iron mordant or to the prussiate to produce a brighter and more purplish tone. The salt probably exerts a reducing action before entering the ultimate compound. Under certain conditions stannic chloride is used. The exact composition of the resulting colours has not yet been ascertained.

Prussian blue is fairly fast to light; it fades under prolonged exposure to sunlight; but according to Chevreul, the colour is restored if kept for some time in the dark. On wool, the colour turns darker on exposure to light. Alkaline or boiling soap solutions readily decompose Prussian blue, leaving brown ferric oxide on the fibre; acids have no action on the colour. Since the introduction of the aniline-blues the use of the colour has considerably decreased.

Cotton.—To dye Prussian blue on cotton, the material is first dyed iron-buff and then passed through an acidified solution of yellow prussiate of potash (or soda); the depth of colour depends on the amount of ferric oxide already precipitated in the fibre; the mordanting and dyeing operations can be repeated alternately to produce a fuller shade. Stannous chloride may be added to the mordanting bath, or (for piece goods) the material can be padded first with stannate of soda and then mordanted with nitrate of iron and stannous chloride. The mordanted goods are passed through a cold or lukewarm solution of 2 parts of yellow prussiate and 1 part of sulphuric acid per 100 parts of dye-liquor; they are finally washed in water and dried.

Wool.—The mordanting and dyeing method does not give satisfactory results on wool and is rarely used. Prussian blue is produced on this fibre without previous mordanting with iron, by decomposition of the acidulated solutions of the prussiates. Before treating the wool with the prussiates, it may be mordanted at the boil with stannous chloride and oxalic acid; or it may be dyed directly with the prussiates. Sulphuric, hydrochloric, and nitric acids are used for acidifying; nitric acid gives the best results with yellow prussiate, probably on account of its oxidising action—about equal quantities of yellow prussiate and of nitric acid (64° Tw.) are used. Nitric acid also makes the colour greener. Generally speaking, sulphuric acid is most satisfactory. Mixtures also of the three acids are used, for instance, 4 measures of sulphuric acid, 2 measures of hydrochloric acid (32° Tw.), and 1 to 2 measures of nitric acid (64° Tw.). The wool is introduced into a cold bath containing about 10 per cent. of yellow prussiate and 20 per cent. of sulphuric acid, the temperature is raised in the space of one hour to the boiling-point, and the boiling continued for a half to three-quarters of an hour. The colour is rendered brighter and more purplish by adding 1 to 2 per cent. of stannous chloride during the last half or three-quarters of an hour of the boiling. Instead of the stannous chloride, "muriate of tin" or "finishing blue spirits," and similar preparations of stannous salts, are used. A process of this kind is still used in some cases for a special kind of goods. The dye-bath is prepared with a cold solution of 12 per cent. red prussiate of potash, $1\frac{1}{2}$ per cent. of tartar, $\frac{3}{4}$ per cent. of tartaric acid (of the weight of the goods), $\frac{1}{2}$ per cent. stannous chloride, and 10 per cent. of Glaubersalt are added. The material is entered at the ordinary temperature. The bath is gradually heated to the boil, and the boiling is continued for 30 to 60 minutes, until the

shade is developed. A dark blue is sometimes produced in a similar way, using, however, only one half that amount of red prussiate and topping afterwards in the same or in a fresh bath with logwood.

The colours thus produced may be detected by the reaction with nitric acid which produces green spots on the cloth.

Silk is now rarely dyed with Prussian blue, except for weighting in black dyeing (see p. 355). The processes which are employed resemble those used for cotton. The silk is first mordanted with ferric oxide, soaped at the boil as described on p. 279, for weighting boiled-off silk, and subsequently dyed with prussiate in an acidulated solution (see p. 281).

A brighter blue, known as "Napoleon's blue," was formerly produced as follows:—The silk is worked for half an hour in a cold bath containing 50 per cent. of basic ferric sulphate (50° Tw.), 10 per cent. of stannous chloride, and 5 per cent. of sulphuric acid; after this, it is wrung out and washed, and then worked for half an hour in another bath, prepared with 10 per cent. of yellow prussiate of potash, 2 to 5 per cent. of red prussiate of potash, and 12 to 15 per cent. of sulphuric acid. The silk is then wrung, and both processes are repeated. Finally the silk is softened and brightened in a cold bath, prepared with 15 per cent. of olive oil and 5 per cent. of sulphuric acid (of the weight of the silk); wrung and dried.

PART IX.

MACHINERY USED IN DYEING.

THE textile fibres are either dyed in the loose state, in the form of slubbing, tops or sliver (after combing or carding), in the yarn (hank, warp, or cop), or, lastly, in the piece.

By far the largest amount of coloured material which comes into the market is dyed in the piece, because this is at the same time the most convenient and the cheapest method of dyeing, less labour and less materials being required to produce a given shade on the same class of material than by any of the other methods.

The dyeing in the loose state, as slubbing or as yarn, is generally done because it is necessary in the production of figured materials containing more than one colour (prints excepted), or of mixed or fancy yarns; but the dyeing is also sometimes done before weaving in the manufacture of high-class goods of *plain* design, in order to produce superior results. The dyeing of loose fibre and slubbing is rendered still more expensive to the spinner and manufacturer by the tendency which the fibres have of becoming matted or felted during the process. In consequence of the matting or felting many of the fibres are torn in the processes which the fibres have to undergo preparatory to spinning. The average length of the staple is thus diminished, which, of course, means a loss.

The dyeing of cotton or wool in the loose state, or of wool in the form of slubbing, is frequently done for the following purpose:—The material is dyed in some dozen or twenty different standard colours, including blacks, blues, reds, greens, yellows, drabs, &c. A stock is kept of each, and the desired shade of yarn is produced in the drawing, previous to spinning by mixing the coloured material with, or without, the addition of undyed material in the requisite proportions. By the juxtaposition of the different coloured fibres in the yarn, a similar effect is obtained as by dyeing to shade. Thus, almost any shade of grey can be obtained in worsteds by mixing in this manner, black and white. In light shades, especially, the colours thus obtained in the finished material are far superior in fastness to light to such as are dyed in the piece. In the manufacture of worsteds, the process of *melanging* has a similar object in view. The slubbing is

printed across in stripes; in the subsequent process of drawing, the colours become mixed with the whites in between the stripes, and an apparently uniformly coloured yarn is the result.

Silk is seldom dyed in the loose state; in most cases it is dyed in the yarn. Sewing cotton, as well as cotton, wool, and silk yarns for embroidery purposes are all dyed in the yarn.

Dyeing of Loose Fibre.—In the dyeing of loose cotton, no special apparatus is absolutely requisite. The material after having been boiled with soda ash or caustic soda and washed, is mordanted and dyed in wooden vessels provided with a false bottom and heated

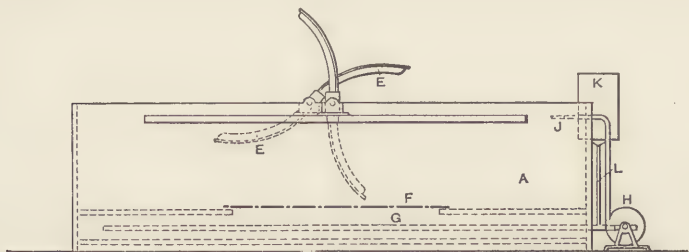


Fig. 59.—Jagenburg's dyeing machine for loose cotton (elevation).

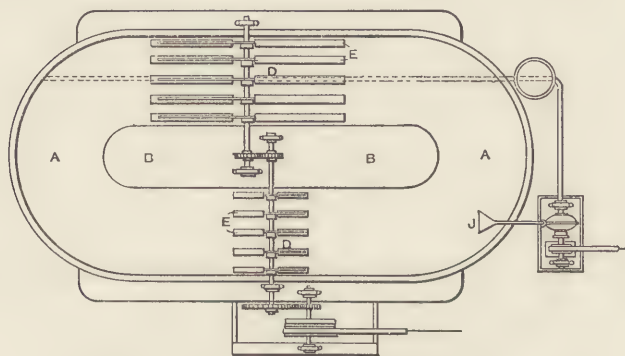


Fig. 60.—Jagenburg's dyeing machine (plan).

by steam, similar to those used in yarn dyeing. There is, indeed, a tendency for the cotton to become matted during the process, thus preventing a free circulation of the dye-liquor, in consequence of which an uneven shade may result; but the unevenness is no longer noticeable after the carding and spinning, so that as long as the shade is right in the yarn, this would be no great disadvantage.

A machine specially devised for the dyeing of loose cotton is that of G. Jagenburg, shown in plan and elevation in Figs. 59 and 60.

The goods to be dyed, which have been previously mordanted (if necessary), are placed in the vessel, A, containing the requisite quantity of water, in which they are stirred continuously by the

stirrers, E, mounted on shafts, D. Near the dye-vessel is placed a centrifugal pump, H, which sucks out the liquor contained in the body, A, of the vessel from below the perforated bottom, F, and throws it in again above. A constant circulation of the dye-liquor is thus effected. Near the pump, H, there is a vessel, K, which is filled with concentrated dye-solution, and is connected with the suction tube, G, of the pump, by means of the tube, L. The concentrated dye-solution thus flows constantly into the suction tube of the pump, becomes instantly mixed in the pump itself with the dye-liquor, and is spurted out evenly and in an attenuated condition through the delivery pipe, J, on to the upper surface of the liquid in the vessel, A.

Another machine which may be used for the same purpose, as well as for loose wool and for yarns, is that patented by Schmidt, and shown in plan and elevation in Figs. 61 and 62.

It consists of two round vats which fit into one another. The outer

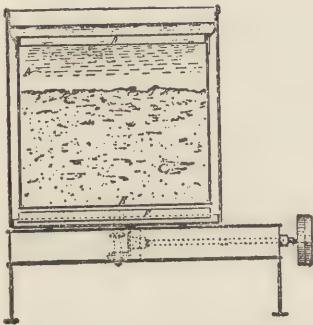


Fig. 61.—Schmidt's dyeing machine (section).

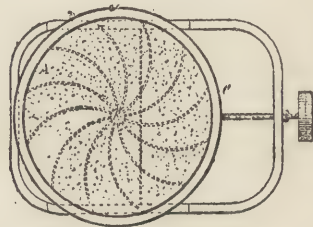


Fig. 62.—Schmidt's dyeing machine (plan).

vat, C, holds the dye-liquor, while in the inner one, A, the material to be dyed is placed.

The inner vat is held by three arms which overhang the edge of the outer vat. It is open at the top, and has in its bottom a number of small openings, which allow the dye-liquor to pass through. The material in this vat, whilst dyeing, is enclosed above and below by copper-wire sieves, in order to prevent it being displaced by the dye-liquor. On the bottom of the outer vat a steam coil is fixed, around which the liquor must pass in rising. By this means the temperature of the dye-liquor and that of the material being dyed is kept almost the same. This is a great advantage which is not met with in other dyeing systems. Between the bottoms of the two vats a turbine or paddle wheel (Fig. 61, F) is placed, which is caused to rotate by bevel wheels driven by a pulley.

By the rotation of this turbine the dye-liquor between the sides of the vats is forced upwards, and on reaching the top rim of the inner or

suspended vat, which is lower than the outer vat, it pours over on to the contents of the former. When the liquid is forced upwards a partial vacuum is formed between the bottoms of the two vats, so that the liquid pouring over the material being dyed forces its way through to the bottom, circulation then commencing again.

In order to add more colour or acid, &c., whilst dyeing, without having to take the material out, as in dyeing in open pans, a pipe is fixed to the side of the outer vat which discharges itself directly on to the arms of the turbine. By this means colour, &c., added afterwards is mixed with the whole of the liquor in the shortest possible time, and, therefore, produces no uneven places in the material. The apparatus can be quickly emptied of excess of dye-liquor by the outlet valve in the bottom. The suspended vat is lifted out by a fixed or running crane, according to circumstances.

Dyeing in this apparatus is in general the same as in others, or in open pans. A considerably smaller amount of water is required than with open pans, and, therefore, some precautions are necessary. The copper-wire sieves which are covered with well-boiled jute or linen cloth, in order to prevent the so-called copper stains produced by acids, keep the material from moving and becoming matted. Before dyeing, the woollen yarn or other material is well scoured and wetted out, and if possible hydro-extracted, so that it absorbs the dye-liquor evenly.

In laying yarn in the vat care should be taken that the layers are always placed in alternate directions; thus, the hanks of the second layer are placed at right angles to those of the first. This point is of importance, as thereby no open channels are left. The heads of the hanks should not be twisted too tightly, but only sufficiently to enable the yarn, when dyed, to be easily taken out. The hanks should not be tightly pressed, but only laid close together. If these simple directions are followed perfectly even dyeing always results.

The Obermeier apparatus (see p. 680) may also be used for the dyeing of loose cotton, but is more especially suitable for loose wool, as in this system the material remains stationary and there is no danger of felting.

Loose wool is usually mordanted and dyed in large hemispherical iron vessels which are heated either by direct fire or direct steam. The material is loosely enveloped in the dye-bath with a coarse net, which when withdrawn brings with it the whole of the dyed or mordanted material. During the dyeing, the material is stirred by means of poles or *stangs*.

After mordanting, dyeing, and washing-off, the material is hydro-extracted and dried. In indigo dyeing, the material is wrung after dyeing in the net, so that the liquor can be run straight back into the vat.

Dyeing of Tops or Slubbing.—Wool intended for the manufacture of worsteds is not dyed in the raw state, it being preferable to dye it in the form of slubbing (*i.e.*, in the combed state). For this purpose, the

tops are unwound and the slubbing is made into hanks, in which form it is dyed. The dyeing of slubbing does not differ essentially from hank dyeing, but the material requires much more care in handling owing to its liability to felt. A certain amount of felting is in many cases unavoidable in the operations of mordanting and dyeing, and this, coupled with the trouble of unwinding the tops and balling them again after dyeing, has called into existence numerous machines in which the tops are dyed as such without having to be unwound. The principle on which these machines are worked is the same as that employed in cop dyeing. The material remains stationary, while the hot mordant- or dye-liquor is either forced or drawn through it.

A simple construction of this kind is that patented by Salt & Stead*

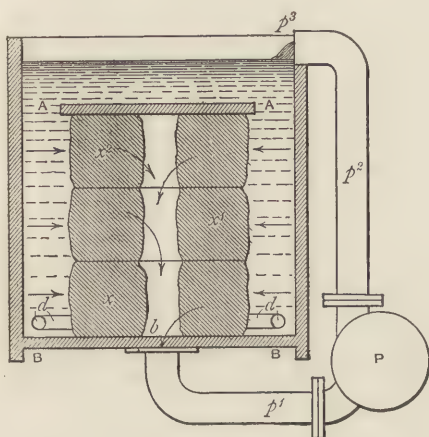


Fig. 63.—Salt & Stead's top dyeing arrangement.

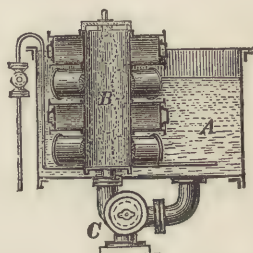


Fig. 64.—Obermeier's dyeing machine for tops.

and shown in Fig. 63. In the figure three balls of tops, x , x^1 , and x^2 , are shown placed in the dye-vat in such a manner that their centres come directly over the pipe, b , at the bottom. A plate, $A A$, is placed on the uppermost ball; d is a steam pipe for heating the contents of the vat. By means of the centrifugal pump, P , the dye-liquor is sucked through the material and delivered back into the vat at p^3 .

An apparatus more generally used is that of Obermeier (Fig. 64), the construction of which varies slightly according to the material to be dyed. For tops it consists essentially of a movable copper cylinder, B , bearing on its circumference 15 to 20 slightly conical receptacles for the tops. The cylinder, B , stands in the vat, A , which is heated by steam, and communicates directly with the centrifugal pump, C .

The receptacles of the so-called "revolver cylinder," B , are first filled with tops and closed with perforated copper lids. This takes about 20 minutes for a machine with 20 receptacles capable of holding 160 to

* English Patent No. 9690, 1885.

300 lbs. of wool altogether. The cylinder is then placed in position in the dye-vat, to which the necessary additions of dyestuff, &c., have been made. Steam is turned on and the pump is set in motion, which causes the liquor to circulate from the vat through the material and back into the vat again. When the dyeing is finished the whole cylinder is lifted out by means of a crane, the tops are taken out, hydro-extracted, put back into the receptacles, and dried by blowing a current of hot air through the cylinder.

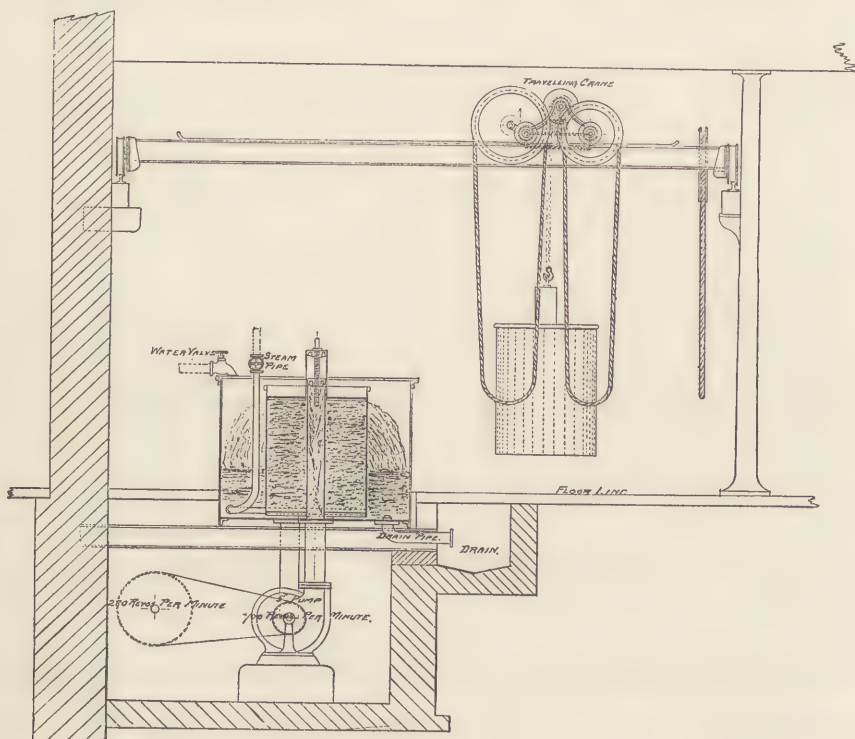


Fig 65.—Obermeier's dyeing machine for loose fibre.

A more general view of the Obermeier apparatus will be obtained from Fig 65, prepared for this volume by the English makers of the machine, Messrs. Mather & Platt. The machine shown in the figure is intended for the dyeing of loose fibre (either wool or cotton) not of tops. In working, it is quite similar to the one previously described, the only difference being that the "revolver" cylinder is replaced by a plain perforated copper cylinder with a wide perforated copper pipe passing up its centre.

Dyeing of Yarn.—This is of much greater importance than the dyeing of loose fibre, and is applied to all classes of textile materials, such as cotton, linen, worsted, woollen, silk, jute, &c. Yarn is gene-

rally dyed in the hank, or in the warp; but cotton yarn is also frequently dyed in the compact form in cops.

Hank Dyeing.—Most yarn is dyed in the hank, because this is the most convenient form in which to deal with it. The usual method of

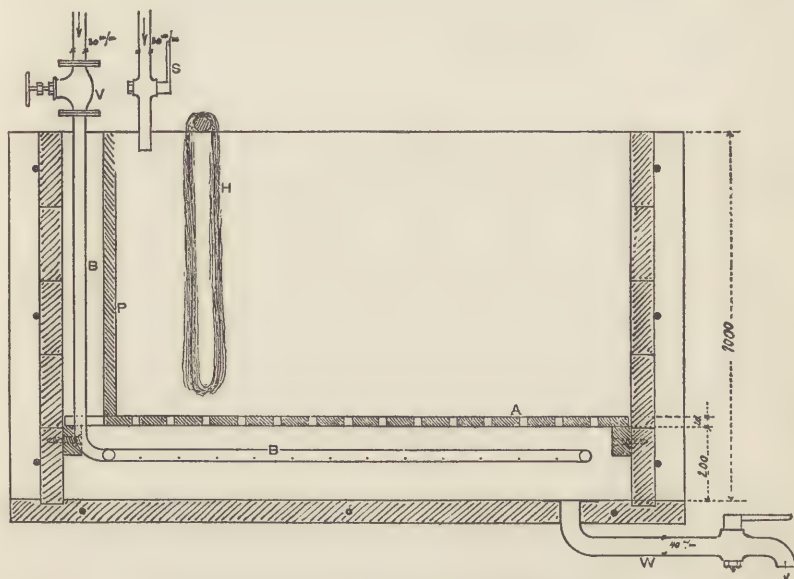


Fig. 66.—Dye-vat for yarn in the hank (section).

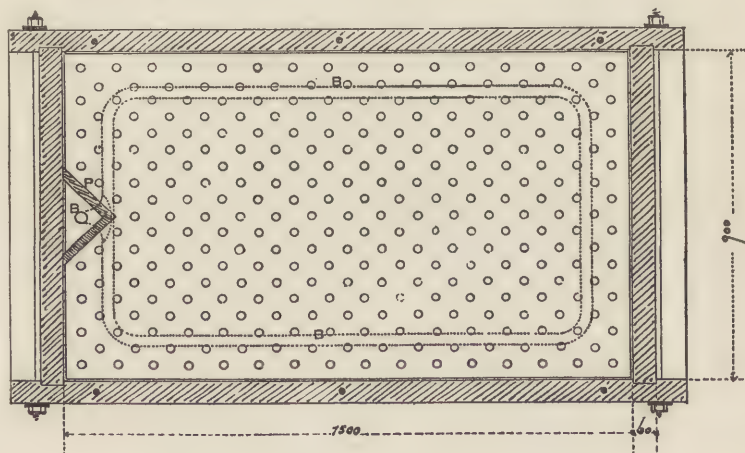


Fig. 67.—Dye-vat for yarn in the hank (plan).

dyeing hanks is very simple. For the mordanting and dyeing rectangular vats constructed of wood (pitch pine is the best), stone (generally Yorkshire flag), or metal (iron, or for silk dyeing tinned copper), and heated by steam, are used. Figs. 66 and 67 show the construction in

section and plan of a wooden vat, such as is ordinarily used in the dyeing of cotton, and of woollen and worsted yarns. It is constructed of strong boards held together by iron bolts, two of which are shown in the plan, while the rest are merely indicated by black dots. A false bottom, A, shown in both figures, serves to protect the yarn from coming in direct contact with the steam. B is the copper steam-pipe, with steam valve, V, which runs round the vat beneath the false bottom, and is here perforated. In passing down to the bottom of the vat, the steam-pipe is cased off by a wooden partition, P. W is the waste pipe, and S the water supply. The dimensions given in the figures are in millimetres.

Stone vats are constructed on a similar principle. They are more durable than wooden ones; they are generally met with in old works. Frequently the false bottom is dispensed with, and the steam-pipe, instead of going all round, is simply a straight pipe passing down the middle of the vat, or two pipes passing at each side from one end of the vat to the other. For many purposes iron steam-pipes serve as well as copper ones, and in these cases the cheaper material is, of course, preferred. The friction of the steam in passing through the perforations widens the latter, and when the holes have become too large, the perforated part of the pipe must be repaired or replaced by a fresh one. For working small vats, as is the case, for instance, in silk-yarn dyeing, the heating is advantageously done by means of a movable steam-pipe with a knee-joint. Several vats may thus be heated by means of the same pipe.

In heating by direct steam the liquor in the vat becomes diluted by the water which condenses from the steam. In the majority of cases this does not much matter; but in dyeing certain colours it is necessary to keep the concentration of the dye-liquor constant. To effect this the vat is heated by a steam coil instead of by direct steam. The steam condenses in the coil, and the water formed is drawn off as it forms.

The top of the vat is usually made to stand at a convenient working height (2 feet 3 inches) above the floor level. Consequently large vats as are used, for instance, in worsted-yarn dyeing, are let into the ground to a considerable depth.

The following is the *modus operandi* adopted in hank-dyeing. The hanks are suspended in rows on smooth sticks or poles, which are laid across the vat, as shown in Fig. 66, H. The second stick-full comes within an inch or two of the first, and so on, until the vat is filled to within about a foot off the end. The hanks are now turned; a workman stands at each side of the vat; one of these passes a rod immediately beneath the stick holding the last lot of hanks; the other takes it, and the whole stick-full is turned a quarter way round, *i.e.*, so that after two turns the parts of the hanks which were at the bottom are now at the top. The stick-full which was about a foot off the end is

now pushed against the end of the vat, and so each set or stick-full of hanks is turned until they come to the other end of the vat. This process is repeated as often as may be necessary during the dyeing or mordanting operation. The number of "turns" during the operation will depend upon the nature of the material and of the dyestuff or mordant employed.

Hank-dyeing Machines.—Much hand labour is necessary in hank-dyeing, and this is one of the principal reasons why the process is so expensive as compared with piece dyeing. Many machines have been devised and patented for doing the hand labour required in turning the hanks automatically. In the majority of machines the turning of the hanks in the dye-liquor is effected by substituting for the dye-sticks a series of porcelain rollers which receive an alternate backward and forward motion, all being driven from one shaft by means of spur wheels, as in the hank-washing machine (see p. 704). In other

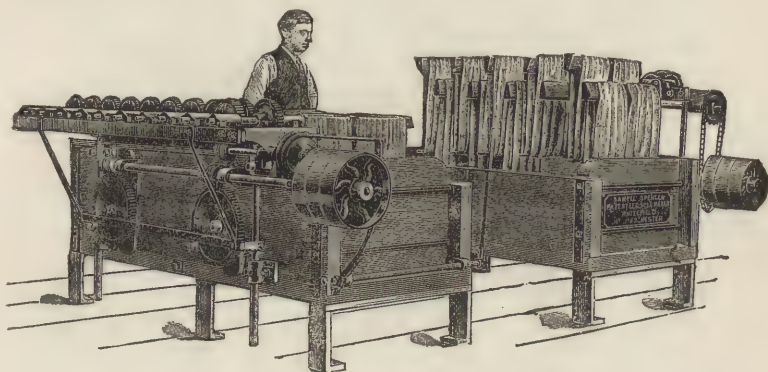


Fig. 68.—Spencer's yarn-dyeing machine.

machines of this kind the shaft is dispensed with, and the motion of the rollers is effected from one to the next by toothed wheels. Fig. 68 shows an arrangement of this kind. All the rollers are attached to a frame-work, which, being raised, removes the whole of the material from the dye-liquor, as shown in the machine on the right-hand side. The hanks are weighted at the bottom by metal rods, in order to keep them straight during the dyeing process.

Another common form of hank-dyeing machine consists of two parallel wheels, which turn slowly in the dye-liquor. The hanks are suspended on sticks at the periphery and near the centre, and according to the depth to which the wheels are immersed in the dye-vat they will be exposed more or less to the action of the dye-liquor. Fig. 69 shows an arrangement of this kind patented by Messrs. Klauder & Bros. Here the whole wheel is encased in a wooden case, so that while the dyeing is proceeding very little steam gets into the room; the material remains hot when not in the dye-liquor, and there is a

saving in steam. By a mechanical arrangement the dye-sticks are also caused to revolve slowly while the machine is in operation.

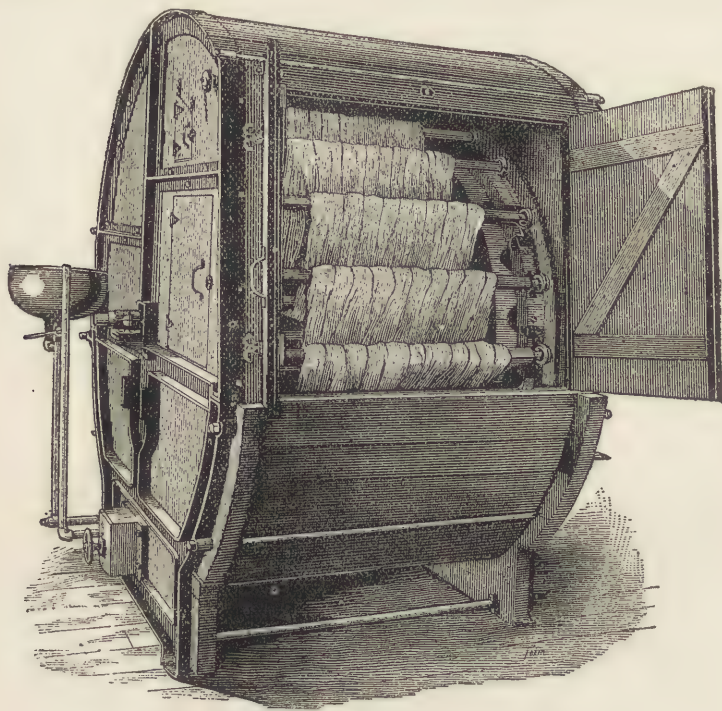


Fig. 69.—Klauder's yarn-dyeing machine.

Another device for causing the dye-sticks to revolve in a system of this kind is due to Messrs. Sykes & Heppenstall of Huddersfield.

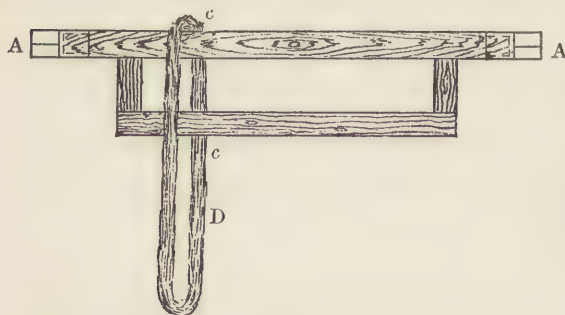


Fig. 70.—Dye-stick for Corron's yarn-dyeing machine.

Loaded discs are placed at the ends of the dye-sticks, which cause them to revolve slowly as the wheel turns in the dye-vat.

Another principle is adopted in the yarn-dyeing machine of C. Corron, which is constructed on a principle,

the object of which is to imitate as nearly as possible the usual hand labour. The dye-sticks, which rest loosely in slots in the sides of the dye-vat, have a framework attached to them (see Fig. 70). By

means of an ingenious, but complicated, mechanical device they are automatically lifted, one after the other, turned, and placed back in the dye-bath, not in the same place, but a few slots further back. By turning the stick right round on its axis, A A, the hanks will be turned by double the distance, c, c , and the point marked D will then be uppermost.

Warp-Dyeing.—

Warps are sometimes dyed in the hank form, but for large quantities, especially of cotton warps, warp-dyeing machines are more advantageous, the dyeing being done much more rapidly and with much less labour than in the hank.

Fig. 71 shows a warp-dyeing machine with three compartments. It consists of a wooden vat divided into three compartments, each of which can be heated by steam. Between each compartment and at the end of the third squeezing rollers are placed, and each compartment is fitted with three copper rollers above and four below. The three compartments may serve to

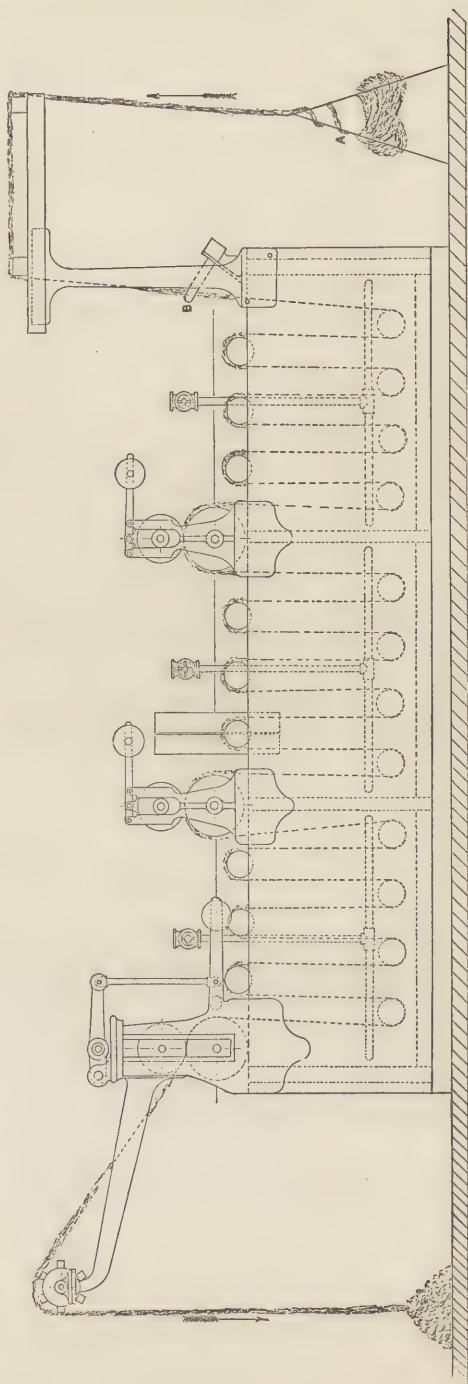


Fig. 71.—Warp-dyeing machine with three compartments (Mather & Platt).

contain three different liquids or they may all contain the same, as may be required.

In the working of the machine, the warps are drawn from the balls, A, pass over two rails above, and through the guides, B (which serve to keep them separate), into the first compartment. Here they pass up and down through the liquid and out through the squeezing rollers into the second trough and so on until they leave the machine through the last pair of squeezing rollers at the end of the third compartment. If the desired shade has been obtained after passing once through the machine, they are said to have been dyed in "one end." Generally, one passage through the machine is not sufficient, and in such cases the warps pass back over lattice-work at the top of the machine into the first compartment again and go through the operation, or series of operations, a second or third time or until the shade is obtained.

Warp-dyeing machines are also constructed with less than three and with more than three compartments according to the special purposes for which they are to be used. The dye- or mordant-liquor or the water used for washing-off is made to pass through the compartments in a direction opposite to that followed by the warps.

Cop-Dyeing Machinery.—As the cotton yarn is formed on the spinning frames, it is wound automatically into so-called "cops." The time and labour necessary for reeling these cops into hanks for the purpose of bleaching and dyeing has been regarded by many inventors as superfluous, and numbers of patents have been taken out for machines the object of which is to dye the yarn in the cop without having to unreel it. Besides effecting a saving in time and labour, the method reduces to a minimum the danger of damaging the yarn. In nearly all these patents one and the same principle is adopted—viz., the dye-liquor is either forced or sucked transversally through the mass of the cop. After the grease and wax have been got rid of by boiling the cops in alkali (see p. 80), this would not appear to present any great difficulty. In practice, however, great difficulties have been experienced, more especially in the production of even shades or colours. Nevertheless, cop-dyeing has during the last few years made steady progress, and there are at present establishments in which large quantities of cotton are dyed in the cop. A great impetus was given to this kind of dyeing by the introduction of the direct cotton colours, most of which possess in an eminent degree the property of dyeing level. It is obvious that only such dyes as are completely soluble in water can be used for the purpose, for if it were attempted to force such a colouring matter as alizarin through the cop, the mass of cotton would simply act as a filtering medium, and, as a consequence, only a very small proportion of the yarn would be dyed, the rest remaining white or at most tinged.

One of the best of these cop-dyeing machines is that devised by Graemiger,* and subsequently improved upon by Graemiger, White-

* Engl. Pat., No. 11,497, 1887.

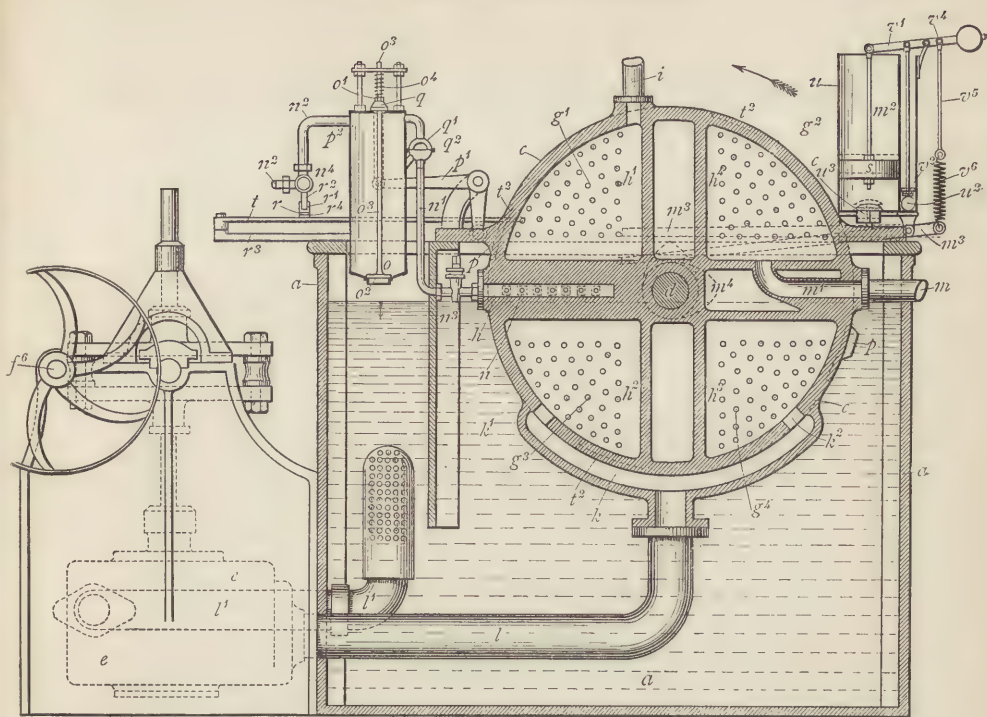


Fig. 72 — Graemiger's cop-dyeing machine (section).

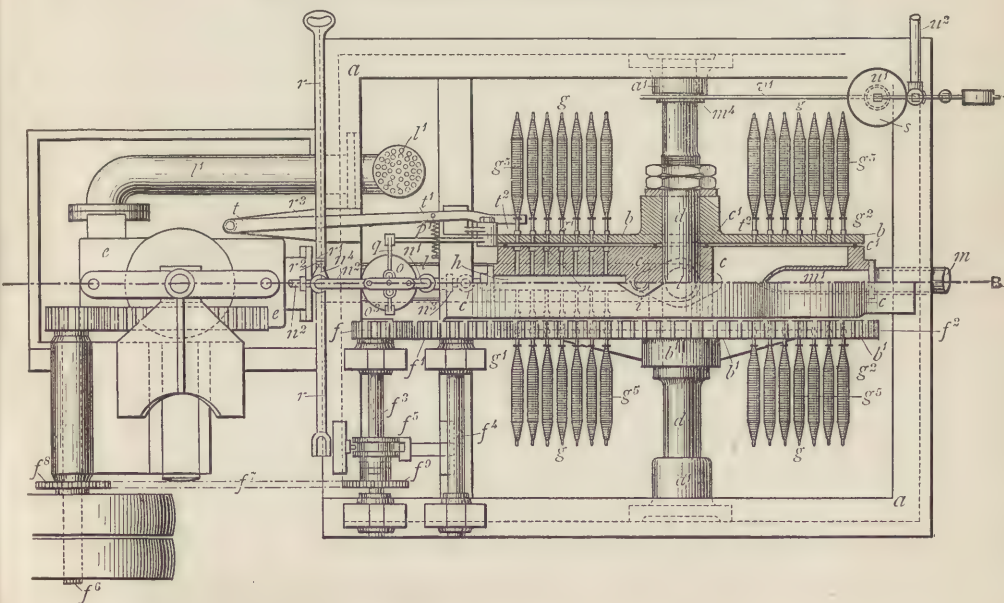


Fig. 73. — Graemiger's cop-dyeing machine (plan).

head, Mason, and Leigh.* Figs. 72 and 73 show section and plan of this machine.

The machine has four chambers, h^1 , h^2 , h^3 , and h^4 , shown in the

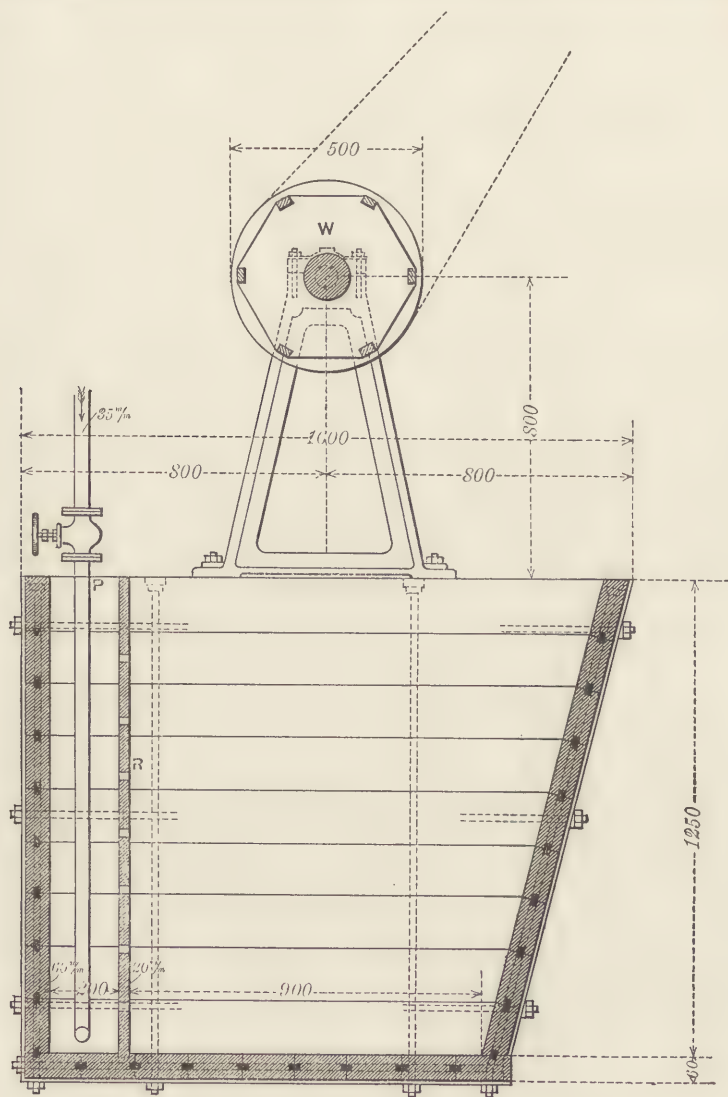


Fig. 74.—Dye-vat and winch for piece goods (cross-section).

section. The two lower chambers are immersed in the liquor of the dye-vat, a , and are connected with a pump which causes the dye-liquor to circulate, being drawn off through the pipe, l , and

* Engl. Pat., No. 9,692, 1889.

re-entering the vat by the pipe, l^1 . Of the two upper chambers, h^1 is connected with an air pump, and h^4 with a liquor pump. The cops are stuck on the cop carrier discs, $b\ b^1$ (plan), which fit hermetically against the walls of the chambers. The discs are fixed on the axis, d , and are intermittently rotated by means of spur wheels, f, f^1, f^2 , shafts, f^3 and

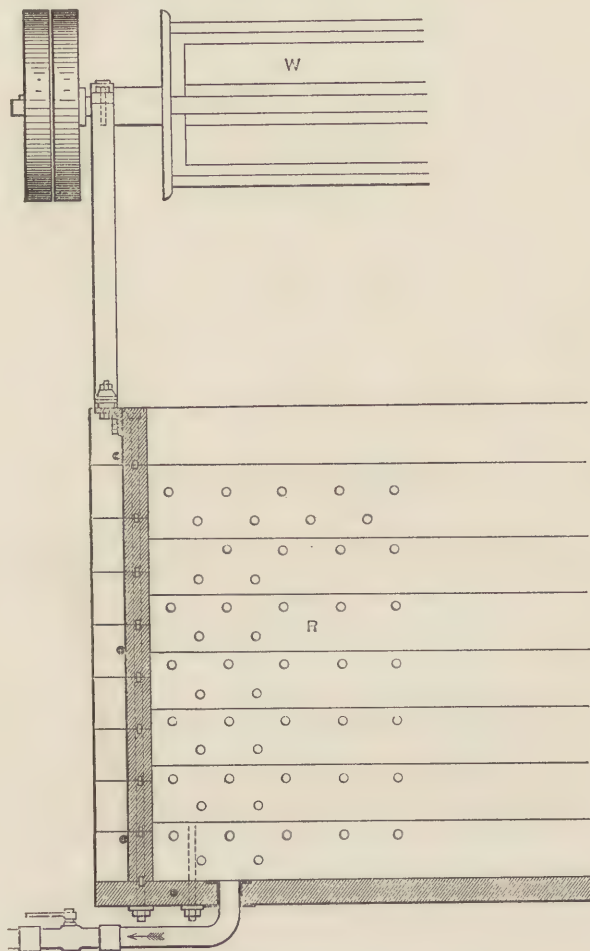


Fig. 75.—Dye-vat and winch for piece goods (vertical section).

f^4 , and clutch, f^5 , from the driving shaft, f^6 , through the chain, f^7 , and wheels, f^8 and f^9 .

The *modus operandi* is as follows:—Those portions of each cop-carrier disc corresponding to the chamber h^1 having been filled with cops, the discs are caused to make a quarter-revolution. The cops thus come opposite chamber h^2 , which being in connection with the suction pump, sucks the dye-liquor through the mass of the cops. With the second

quarter-revolution the cops come opposite chamber h^3 , when practically the same takes place as in chamber h^2 . With the third quarter-revolution the cops are brought opposite chamber h^4 where the superfluous dye-liquor is drawn off through the pipe m^1, m . With the fourth quarter-revolution, lastly, the discs are brought back again to their original position. They are removed and replaced by fresh ones. The dyed cops are dried in another apparatus by sucking hot air through them.

Piece Dyeing.—In cotton, woollen, and worsted goods and in

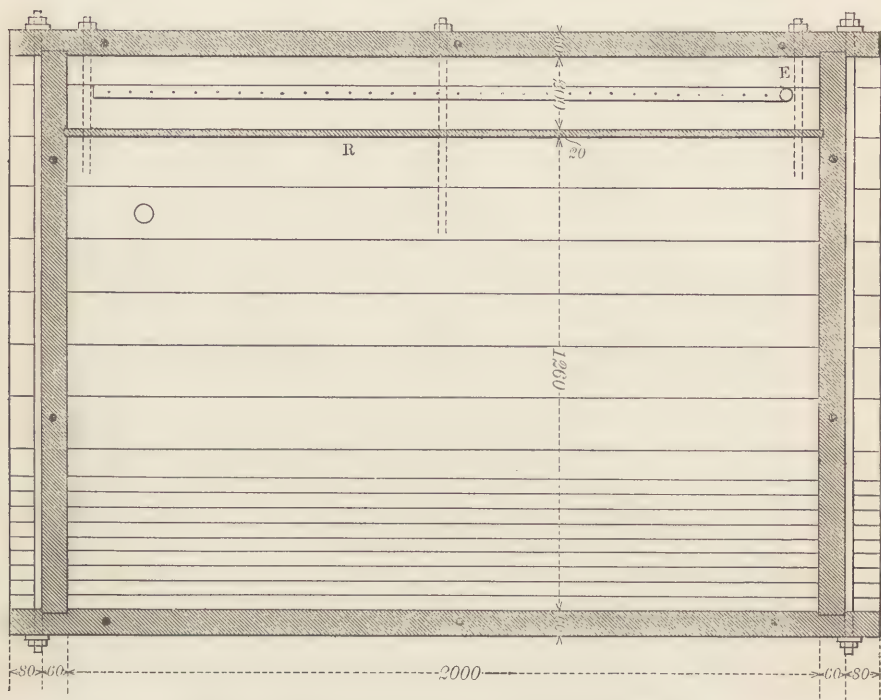


Fig. 76.—Dye-vat and winch for piece goods (plan).

mixed fabrics, dyeing in the piece by far exceeds in importance the dyeing of these materials in any other form.

Piece goods are almost invariably dyed by machinery, except in job-dyeing, where much hand labour is still used.

The simplest form of machine for dyeing pieces is the dye-vat and winch. The construction of a machine of this kind is shown in cross-section, vertical section, and plan in Figs. 74, 75, and 76, in which the measurements are given in millimetres, and are calculated for a machine capable of dyeing about 220 lbs. of woollen cloth. The vat is constructed of wooden boards held together by iron bolts, some of which are shown, while others are merely indicated by black dots. The

heating is done by direct steam by means of the copper pipe, P, which enters at one end (at E) and runs along the whole length of the vat. A perforated wooden partition, R, serves to keep the pieces from coming into direct contact with the steam-pipe. V is the waste-pipe.

By means of the winch, W, the pieces stitched together so as to form an endless band are caused to circulate continuously through the dye-liquor during the operation of mordanting or dyeing. Frequently the pieces are arranged on the same winch in the form of several endless bands, parallel to each other and separated by lattice work, so as not to become entangled. Here the winch is shown to be driven by belt and pulley, but in many works this is still done by hand by means of a handle. In a machine of this kind, all the operations of scouring, mordanting, dyeing, and washing-off may be effected.

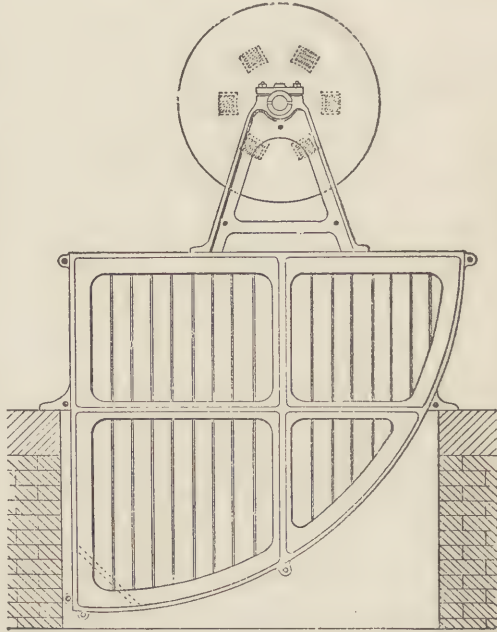


Fig. 77.—Dye-vat and winch.

Another form of dye-vat largely used in woollen and worsted piece dyeing is that shown in Fig. 77. The bottom is curved in place of being flat as in the previous construction.

Fig. 78 shows another similar arrangement by Messrs. Mather & Platt more adapted for dyeing heavy cotton goods in colours, and known as a *jig winch*. The same machine may also be used for washing-off after dyeing in jiggers, and for dyeing small lots of warps. To the same firm, the authors are indebted for an engraving (Fig. 79) of their copper-cased dye-beck, in which the heating of the liquor is effected by the admission of steam into the hollow space at the bottom of the vat, a dilution of the dye-liquor during the dyeing operation thus being avoided. This is necessary in certain special cases, such as the dyeing of aniline-black or of the direct cotton colours.

Another form of machine largely used for cotton pieces, especially in alizarin dyeing, is shown in vertical section, side view, and cross-section in Figs. 80 and 81. This dye-vat is constructed of cast-iron.

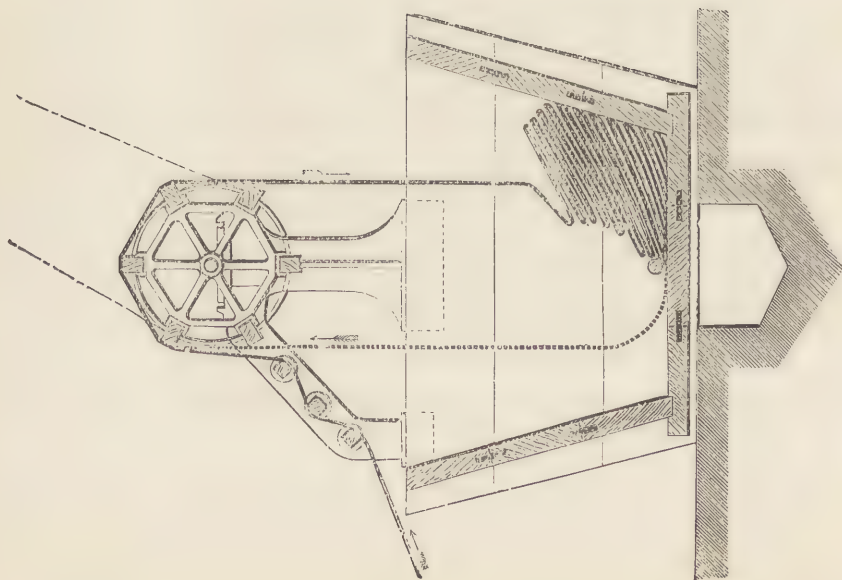


Fig. 78.—Jig winch.

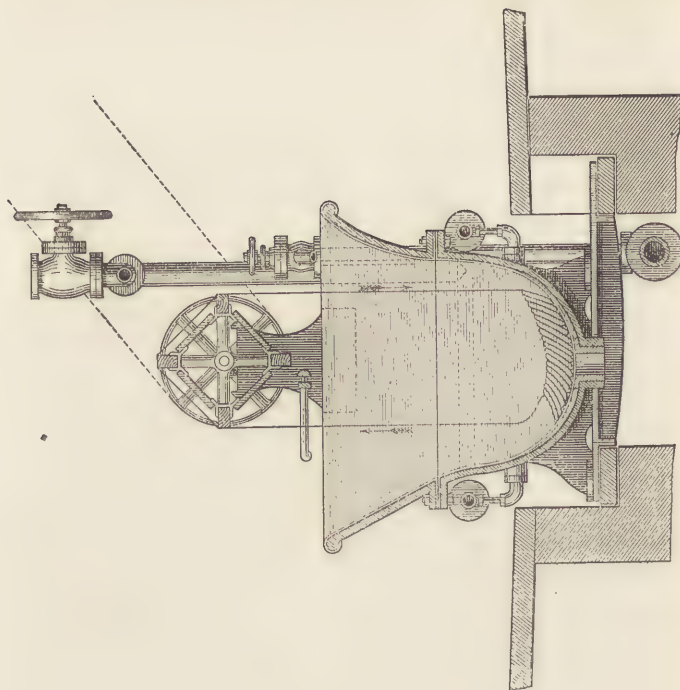


Fig. 79.—Copper-cased dya-beck (Mather & Platt).

The pieces stitched together end to end enter at the left-hand end of the machine (Fig. 80), pass over the winch down into the dye-liquor,

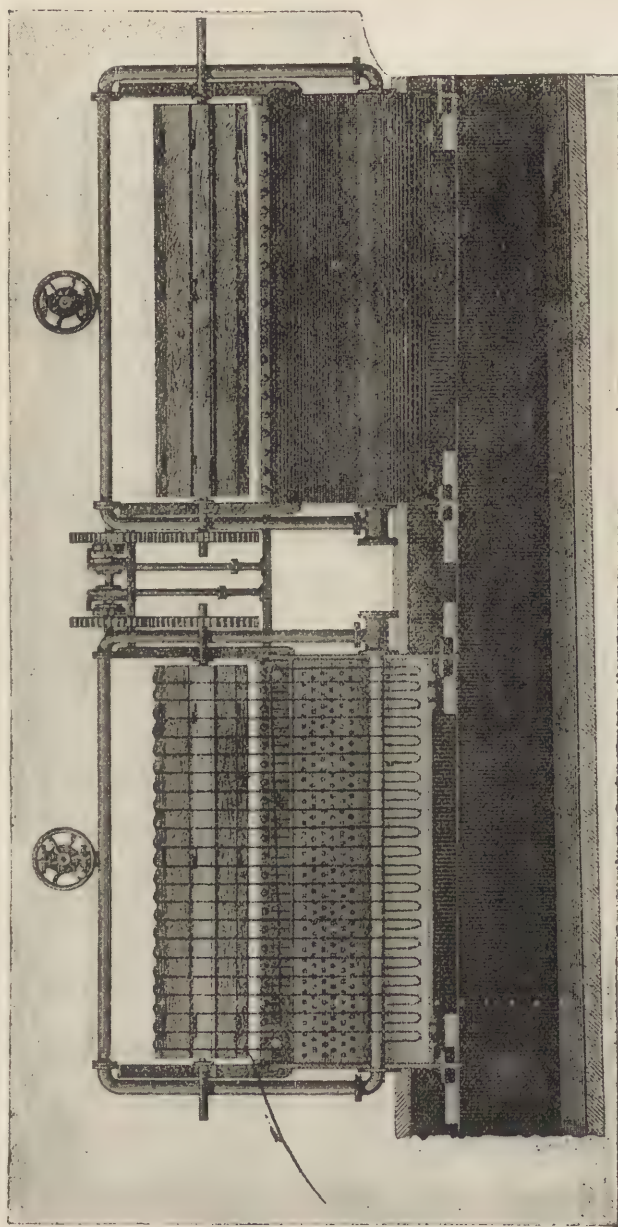


Fig. 80. — Dye-beck for cotton pieces (Mather & Platt).

in which they are caused to remain for a short time by allowing them a certain amount of slack. Thence they are drawn out again, passing between the first and second guide pegs over the winch again and

so on, thus traversing the whole machine in a spiral form. When the first piece has arrived at the end of the winch, it is passed back again over a small roller shown in the figure, and over another roller at the other end to where it entered, and is there stitched to the end of the last piece, thus forming an endless band. A machine of ordinary dimensions is capable of taking 20 to 30 pieces at a time.

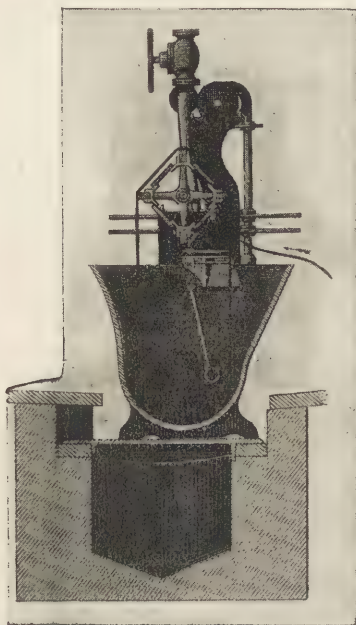


Fig. 81.—Cross-section of Fig. 80.

A machine which imparts to the pieces a double movement in the dye-bath, and which is said to be specially suitable for the dyeing of pile-fabrics is that devised by C. Corron, and shown in Fig. 82. The driving gear not only causes the winch to revolve by means of the chains, A and A', but imparts to it simultaneously by the crank-wheel, C, and the connecting-rod, B, a to-and-fro motion. The manner in which the pieces pass through the dye-vat is clearly indicated by the section in Fig. 83.

The machine which is used perhaps the most extensively in the dyeing of cotton piece goods (also sometimes in bleaching and in dyeing the cotton in mixed fabrics) is the so-called *Jigger*, shown in cross-section in Fig. 85.

Fig. 84 shows a view of two dyeing jiggers, in one of which part of the side is broken away to show the manner in which the pieces pass through. This is also shown in the section. The modern jigger consists of a wooden or cast-iron dye vessel heated by steam and provided with water supply and waste-pipe. In the vessel are three rollers, R, at the top and two, R', at the bottom, which guide the pieces in their passage through the dye-liquor. In the section they are being drawn from roller B on to roller A, passing twice down and up through the dye-liquor before reaching A. During this passage the roller A is driven by a bevelled wheel from the driving shaft (Fig. 84), the pieces being kept in a state of tension by means of a brake (shown in Fig. 84) on roller B. When roller B is empty the order is reversed; B is then connected with the driving shaft, and the brake is put on A. This alternating action goes on until the pieces are dyed, when they are run straight off on to the "batch roller," W, which may be placed on either side of the jigger as may be desired.

For colour dyeing, the jigger is a most convenient form of machine.

The pieces pass through at their full width, and do not remain for a long time in the dye-liquor. As the dyer can conveniently approach the machine from any side, he can at once see how the operation is going on.

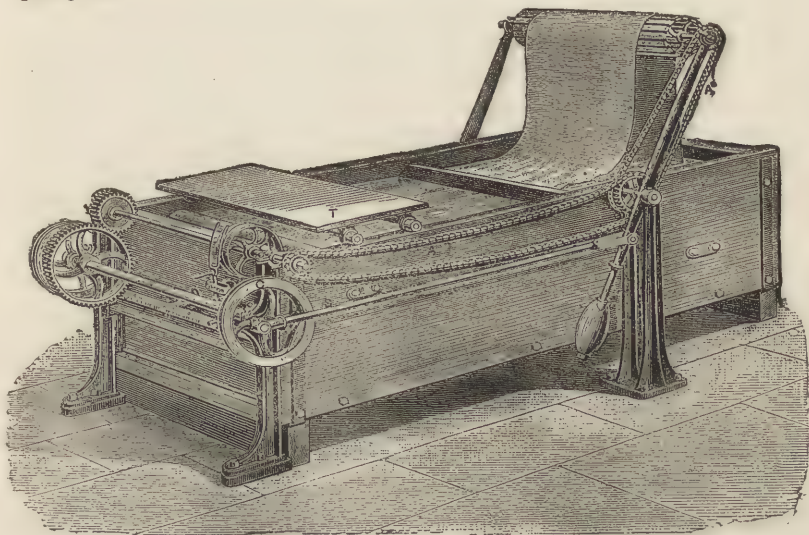


Fig. 82.—Corron's piece-dyeing machine.

After the pieces have been "batched," it is not advisable to allow them to lie in one position for any length of time, as the dye-liquor which they retain mechanically would sink by gravitation to the bottom, and the lower layers would be liable to become dyed a darker shade than the upper ones, thus giving rise to unevenness. It is best to wash off as soon as possible after dyeing.

Padding Machines.—The use of padding machines is almost entirely restricted to the treatment of cotton piece goods, either for dyeing them in the concentrated solution of some colouring matter (*e.g.*, crocein-scarlet), which has little affinity for the cotton fibre, or for preparing with various mordants which are afterwards fixed by ageing or otherwise. In principle, the construction of an ordinary padding machine is very simple. It consists essentially of a vessel (Fig. 86) of comparatively small size holding the colour or mordant solution, and a pair of squeezing rollers. The pieces are drawn from the batch roller through the liquid in the vessel or trough and thence through the squeezing rollers superposed. The excess of liquid is

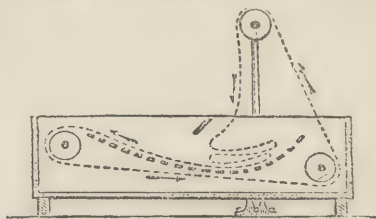


Fig. 83.—Section of Corron's piece-dyeing machine.

thus uniformly expressed, and the pieces are either batched again on the other side or pass away directly to another operation.

Padding machines may also be employed for dyeing in place of jiggers, by increasing the size of the vessel A, and providing a larger number of rollers by which the pieces are caused to pass several times up and down through the liquor. When batched after having passed through the squeezers, there is less danger of the pieces becoming uneven through after-dyeing.

For padding on one side only (slop padding), a single-colour printing machine is frequently employed.

The piece passes round the large iron roller, A (the bowl), which

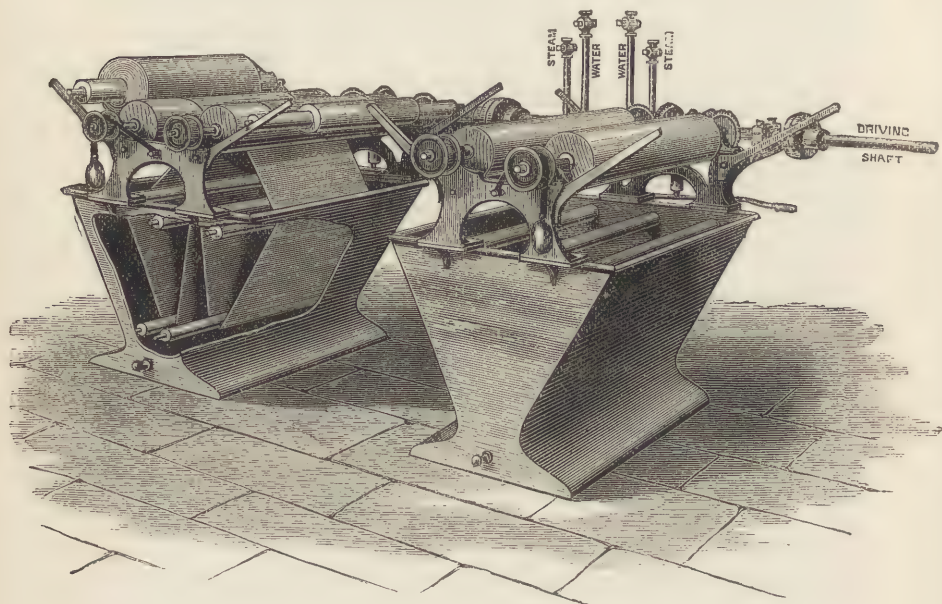


Fig. 84.—Dyeing jiggers (Mather & Platt).

presses against the copper or brass printing roller, B (Fig. 87). The latter presses against the wooden colour roller which runs in the thickened colour or mordant contained in the colour box, C. The whole surface of the printing roller is engraved diagonally with fine intermittent lines in such a manner as to enable it to take up more or less of the colour (according to the depth of the engraving). By means of a smooth steel blade or "doctor," D, the excess of colour is scraped off the printing roller, which retains, after having passed it, only what colour remains in the engraving. This becomes transferred to the piece at the contact of B and A, impregnating the latter with the colour in a uniform manner. Between the piece and the bowl there passes an endless band of thick felt, E (the blanket), the object of which is to provide an elastic layer between the bowl and printing roller. Between the

blanket and the cloth to be printed a "back-cloth" is usually run in order to prevent the blanket from becoming soiled.

Indigo-vats.—For the dyeing of indigo on yarn, wood or stone vats are generally employed which are deeper than, but otherwise practically identical with, those used for ordinary dyeing purposes. For dyeing loose wool and heavy woollen fabrics in the "woad-vat,"

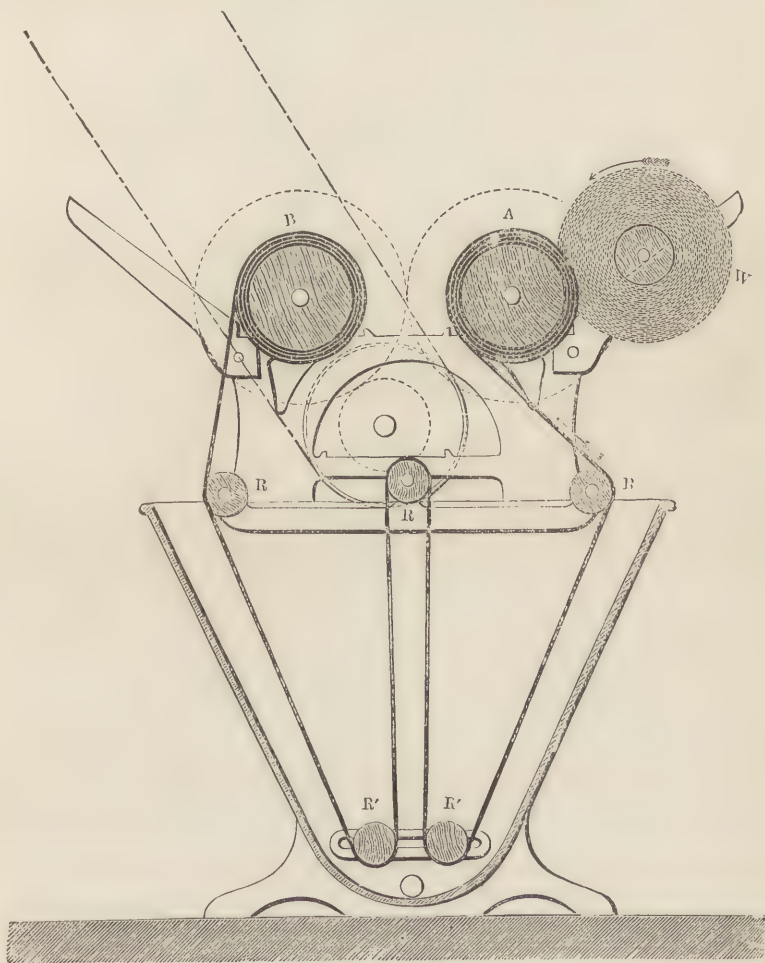


Fig. 85.—Dyeing jigger (section)—Mather & Platt.

large circular iron vats, about 6 to 10 feet deep and 6 to 7 feet in diameter, are used. They are usually built round with brick-work, with an annular space for the admission of steam, and are let into the ground to a considerable depth. Double-cased iron vessels are also sometimes used.

A special machine which is largely used for the dyeing of cotton

pieces is shown in section and plan in Figs. 88 and 89. It consists essentially of a large cast-iron tank divided into two compartments.

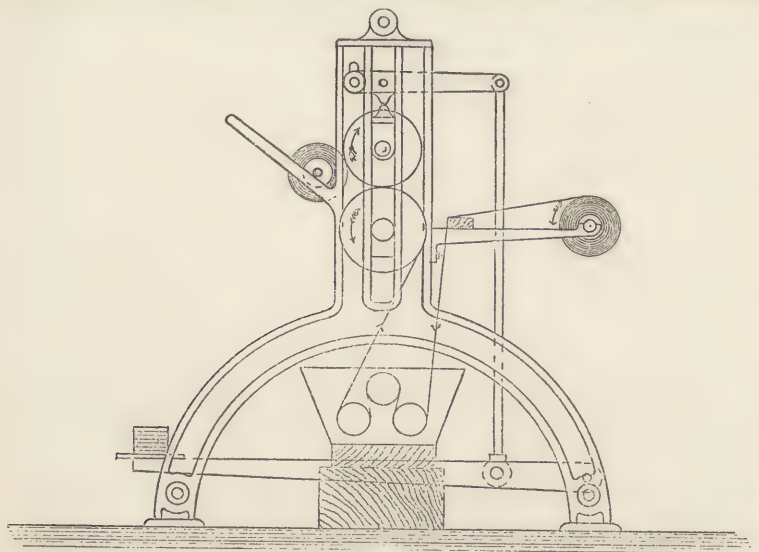


Fig. 86.—Padding machine.

Each of these contains a series of guiding rollers which are mounted on a framework; the latter can be taken out for the purpose of cleaning the vat. At the bottom of each compartment there is a mechanical stirrer, by means of which the sediment can be stirred up in freshening up the vat. The course which the pieces pursue in being dyed is shown in the figure (88) by means of arrows. They pass from the table on which they are piled at full width over the top of the machine through the stretching rollers into the first compartment (on the left), thence into the second, and through the squeezing rollers at the end. From there they pass up and down over the rollers held by the framework fixed above the vat (in order to allow the indigo to oxidise in the

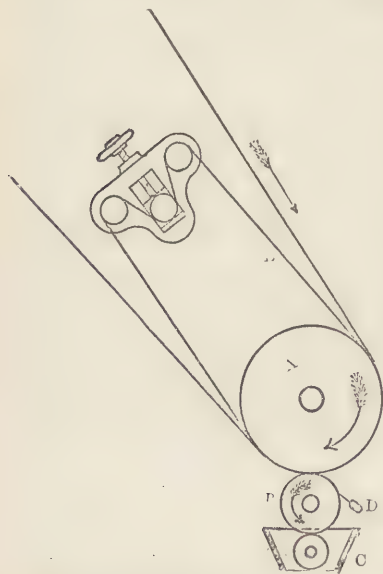


Fig. 87.—Single-colour printing.

fibre) and thence over the top back through a pair of nipping rollers and on to the table again. The advantages of this vat over the

ordinary ones are that it can be readily cleaned and the oxidation of the pieces requires very little space.

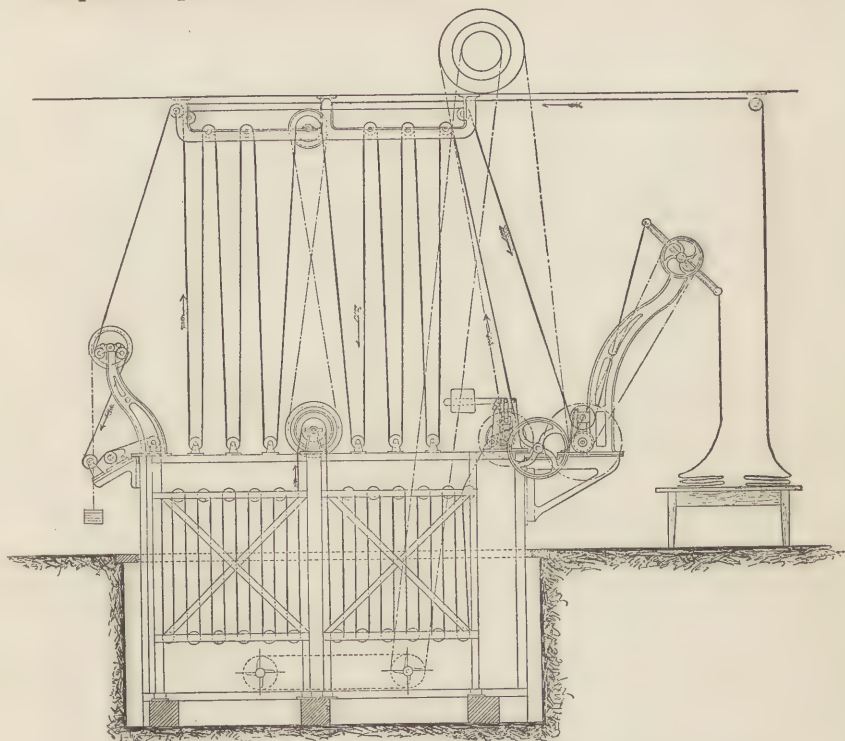


Fig. 88.—Continuous indigo-dyeing machine (E. Welter & Co.)—(section).

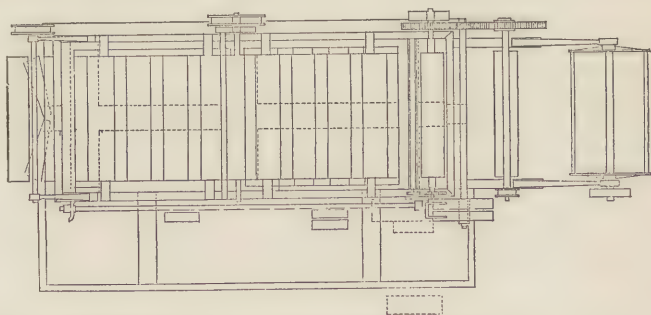


Fig. 89.—Continuous indigo-dyeing machine (E. Welter & Co.)—(plan).

Extracting of Dyewoods.—The addition of the necessary materials to the mordant or dye-bath is generally made at the beginning of the operation. In dyeing to shade a smaller quantity is added than that which is required to produce the full shade, the rest being added towards the end of the operation in “matching off.”

Soluble coal-tar colours, extracts, and paste colours may be added

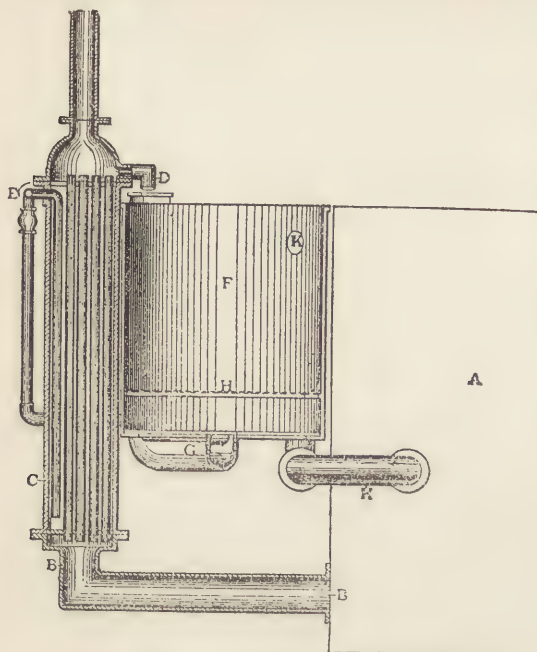


Fig. 90.—Smithson's dyewood extractor (section).

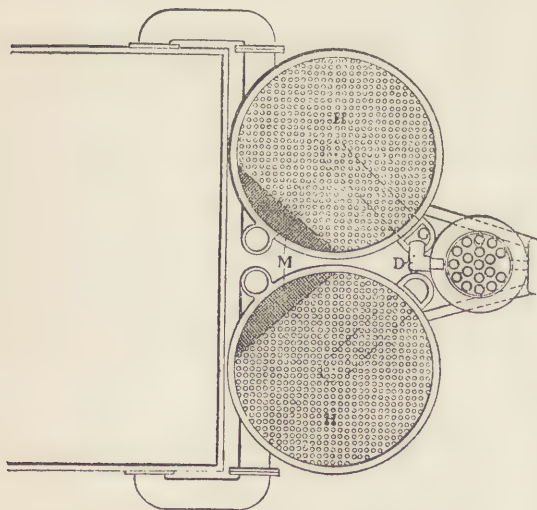


Fig. 91.—Smithson's dyewood extractor (plan).

to the dye-bath at once, or, if they are apt to "flush"—*i.e.*, to go on too rapidly and thus cause unevenness—they may be added by degrees. In the dyeing of wool, dyewood extracts (especially logwood extracts) are not largely employed, practical experience having shown that better colours are obtained by using the chipped or ground dyewoods; this method is at the same time considered more economical. It is not advisable to add the chipped or ground wood to the dye-bath in the loose form, as it would adhere mechanically to the material, and some trouble would have to be taken to get it out again. A common method of overcoming this difficulty is to put the amount of dyewood or dyewoods necessary for the desired shades in bags, and allow them to boil for 20 minutes or so in

the vat before entering the goods. Once boiling is, however, not

sufficient to extract the colouring matter, and, in order to avoid a loss in this manner, it is usual in many works (especially in black dyeing) to boil the bags three times—*i.e.*, in preparing the bath one bag is used containing fresh colouring matter, one which was imperfectly extracted in the operation before, and one from the last operation but one (see p. 345).

An ingenious device for completely extracting the dyewood, and at the same time heating the dye-vat and causing a circulation in it, is due to Mr. S. Smithson.* The apparatus (shown in Figs. 90 and 91) consists essentially of a pair of extracting vessels, F, constructed of cast iron, and provided with false bottoms, H, which are attached to the side of the dye-vessel, A. From a point a few inches above the bottom of the dye-vessel there passes a pipe, B, which has a through connection with the nozzle, D, through a number of tubes or pipes shown in both

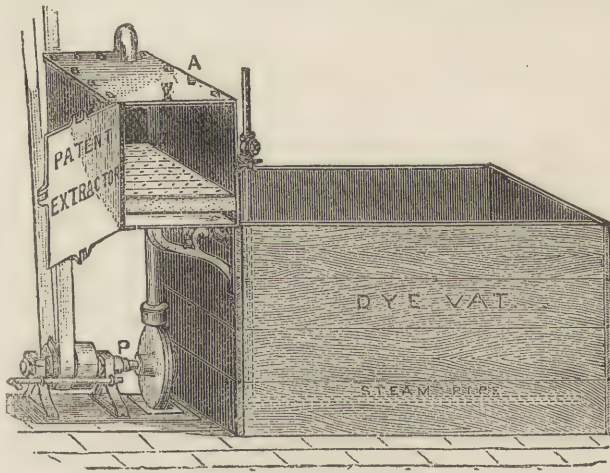


Fig. 92—Dye-vat and extractor.

figures. These pipes are enclosed in a steam-tight cylinder, C, into which high-pressure steam is admitted when the machine is in operation. The dye-liquor in the vat finds its own level in the tubes connected with B, and, becoming here heated to boiling, the liquid expands, and rising above the flange, E, finds an outlet at D, and empties itself into either of the pipes, G, according to the direction which may have been given to the nozzle. The boiling liquor passes down the pipe, G, and, entering the extractor at the bottom, rises slowly until it reaches the point, where it passes out and back into the vat again through the pipe, K'. Sieves, M, prevent bits of dyewood getting into the pipe, K. A continuous circulation is thus established, by means of which the wood is completely extracted. Two extractors

* Whilst this portion of the work is going through the press, Smithson has introduced an improved machine for the same purpose. A description of it is given in the *Journ. Soc. Dyers and Col.*, January, 1893.

are provided, so that while one is being used, the other can be emptied and refilled.

Another form of machine for the same purpose is that devised by F. Rhodes, and shown in Fig. 92.

The chipped wood, or woods, to be extracted are placed in the box, A, the door of which is then screwed up. The hot liquor from the vat is then caused to circulate through the box by means of the centrifugal pump, P. Bits of dyewood are prevented from getting into the vat by the false bottom and sieve placed at the bottom of the box.

In large works the dyewoods (principally logwood and fustic) and tannin substances are sometimes extracted under pressure in large wrought-iron extractors, and the liquors are conducted by means of pipes from the reservoirs in which they are stored, into the dye-house. The system is both convenient and economical.

Operations after Dyeing.—Steaming.—In textile printing, this is a most important operation, as most of the colours are fixed in this way. But in dyeing, steaming is only made use of in one or two special cases, as in the production of alizarin-reds, Turkey-red, and aniline-black (*q.v.*).

Washing.—After mordanting or dyeing, the goods are usually washed in water for the purpose of removing the excess of mordant or dye-solution which they mechanically retain. This is necessary after mordanting in order to prevent any of the mordant getting into the dye-bath, for if this occurred some colour would be lost through the formation of an insoluble lake in the dye-bath and not on the fibre. After dyeing, washing-off is generally necessary in order to cleanse the material from excess of colour and additions to the dye-bath.

In some cases, as in the mordanting of silk with tin or iron, the washing-off has besides the effect of fixing the mordant.

The operations of washing and the construction of washing machines have already been dealt with under the heading Washing and Bleaching (p. 74), and most of the machines described there could be used equally well for washing-off after mordanting or dyeing.

Loose Fibre.—The washing of loose fibre is generally done in the vessel in which it has been mordanted or dyed by letting off the liquor and stirring after having filled with water. A machine which may serve the same purpose is that of Jagenburg (see *Dyeing of Loose Fibre*, p. 676).

Yarn.—The washing of yarn has hitherto generally been done by hand. In the form of *hanks*, yarn is simply rinsed in clean water, two or three turns being, as a rule, sufficient. If running water is at hand it is certainly preferable for washing than the use of a vat or tub. Worsted yarn or slubbing is “showered” after mordanting or dyeing by running a stream of water over the material suspended on rods resting upon a wooden frame, through a large sieve.

Since much labour is required in washing by hand, many machines have been constructed to replace hand labour, and of these some are quite capable of doing so. One machine (Haubold) has already been described under *Bleaching* (Fig. 20, p. 78). Two other washing machines specially designed for cotton yarn in the hank are shown in Figs. 93 and 94.

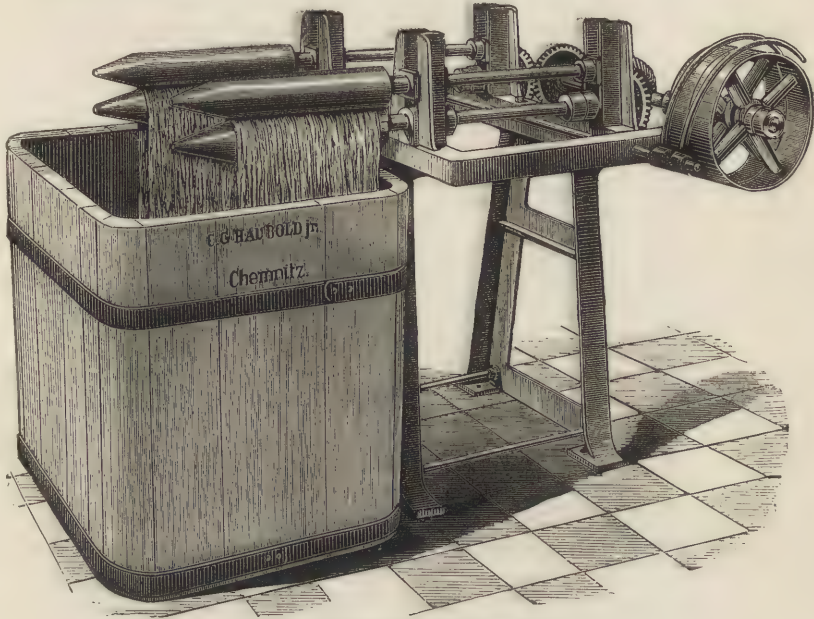


Fig. 93. — Hank-washing machine.

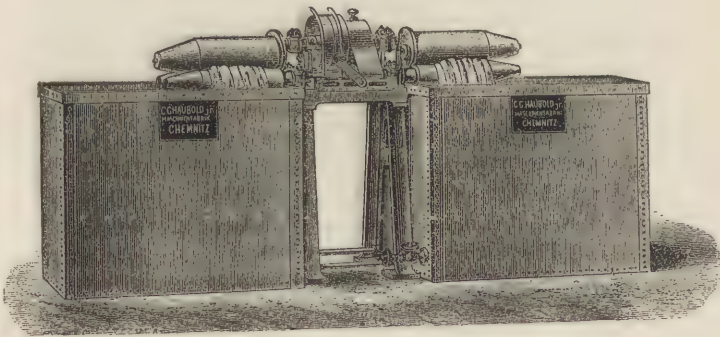


Fig. 94. — Hank-washing machine.

The machine shown in Fig. 93 contains two sets of rollers tapered conically at their ends. The lower ones are caused to revolve by spur wheels from the gearing shown in the figure. On these the upper rollers, the bearings of which run in slots, rest with their own weight. The hanks placed between the two are turned in the water contained

in the washing vessel, and simultaneously squeezed. Fig. 94 shows a similar arrangement, in which, however, one heavy roller, T, serves

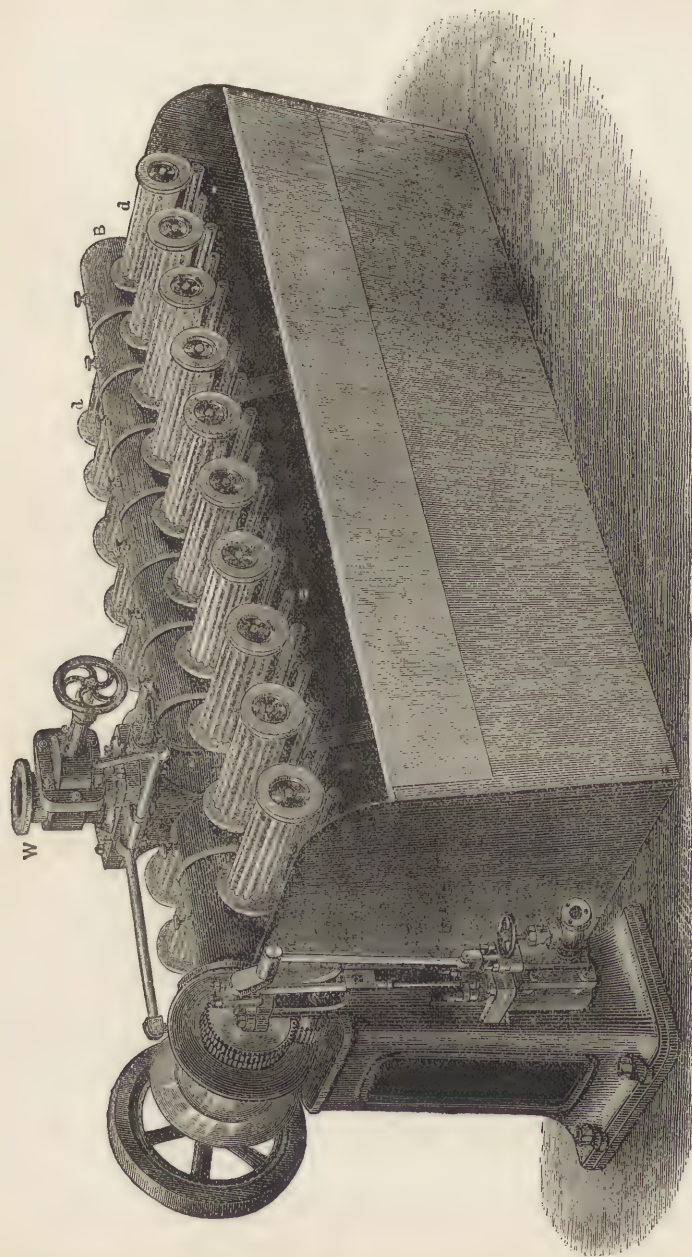


Fig. 95. — Hank-washing machine (Berchtold).

to express the liquid from the hanks borne by two smaller ones running beneath it.

Quite a different form of hank-washing machine is that constructed by Berchtold (Thalweil, near Zurich), and specially designed for the washing of silk hanks, but also applicable for hanks of other materials. A view of the machine is shown in Fig. 95, while Fig. 96 shows a section of two of the rollers.

The machine consists essentially of a double row of porcelain rollers, *d*, on which the hanks to be washed are suspended, and which receive, through the gearing at one end of the machine and the worm-gearing in the boxes, B, an alternate backward and forward motion. Whilst the hanks, *a* (Fig. 96), are being thus turned backwards and forwards,

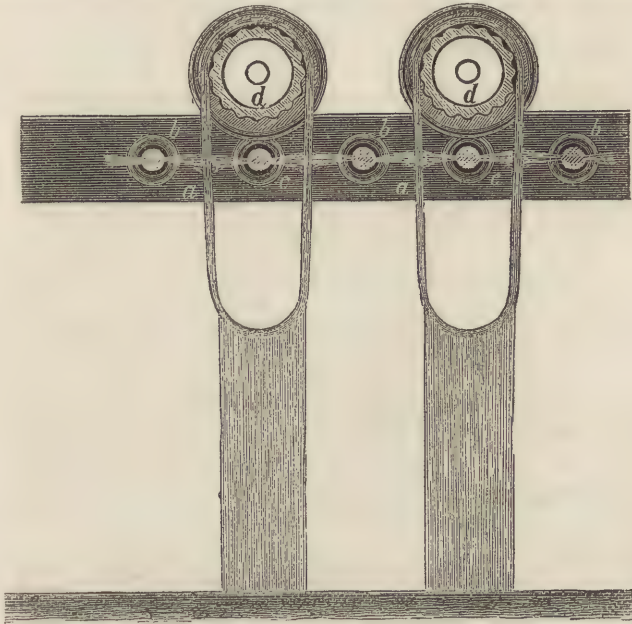


Fig. 96.—Hank-washing machine (details).

they are thoroughly washed by jets of water (admitted from the main by the valve, W) which emanate from the perforated pipes, *b* and *c*, placed so as to come alternately inside and outside of each hank. In some machines, similarly constructed, the water emanates from perforations in the porcelain rollers.

Yarn in the *warp* is washed in the same machines as those employed for mordanting and dyeing.

Pieces.—The washing of pieces is almost invariably done by machinery. Several machines for this purpose have already been described under Washing and Bleaching (*q.v.*). For woollen and worsted goods the dolly and broadwashing machine are mostly employed. Several of the piece-dyeing machines described may also be used for washing-off. Another form of washing machine used specially

in the washing of cotton pieces is the so-called square-beater washing machine shown in Fig. 97, and in section in Fig. 98.

The pieces, stitched together end to end, pass into the machine at A in rope form and, following the course indicated by the arrows in the section, pass first round the winch roller, B, thence through the squeez-

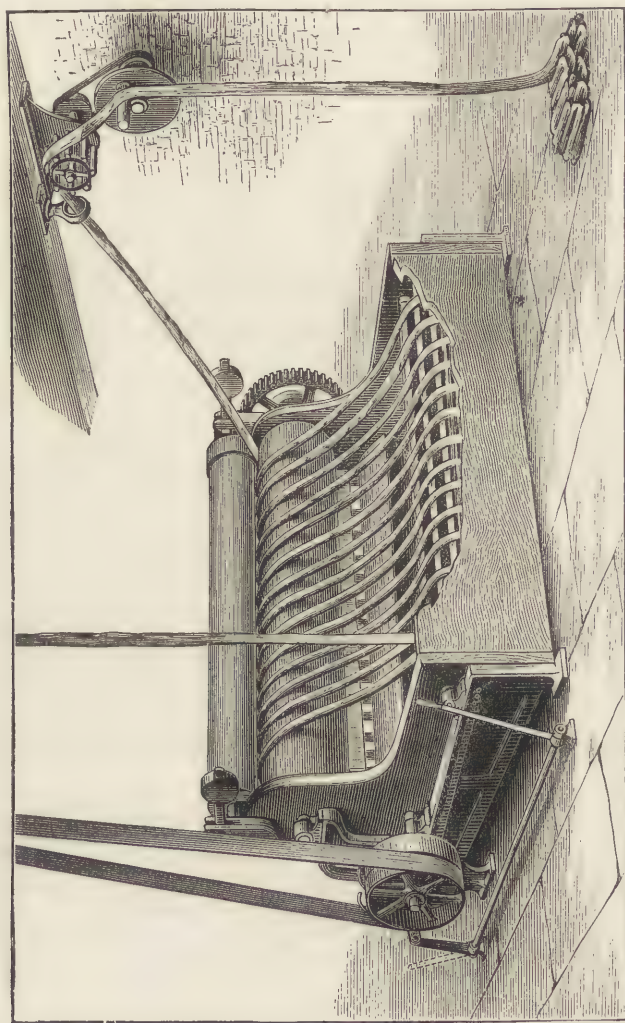


Fig. 97.—Square-beater washing machine (Mather & Platt).

ing rollers, R, R¹, past the square beater, S, through the water back to B, following the same course over and over again in a spiral direction until they leave the machine at the other end, and are drawn off by the winch, W. In passing the square beating roller (shown in the section as being driven by spur gearing from the squeezers, while

in the view it is driven direct from the fast pulley, the squeezers in this case being driven by spur gearing), which revolves in a contrary direction to that followed by the pieces, the cloth opens out from the rope form to almost its full width in passing underneath and along the surface of the water, and receives at the same time a flapping

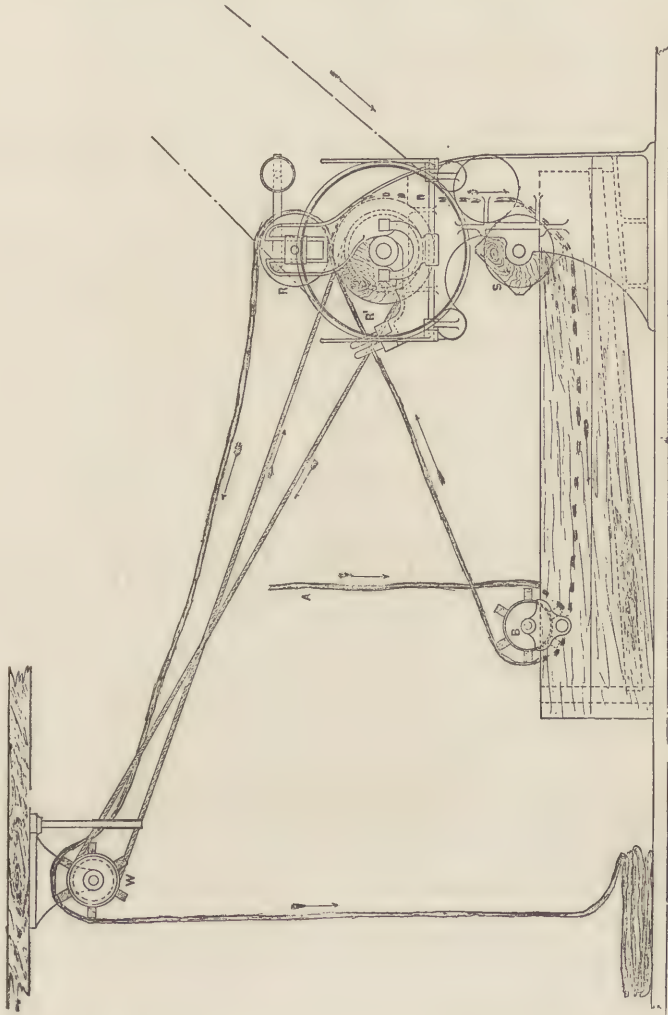


Fig. 98.—Square-beater washing machine (section).

motion. The washing is thus done at a high speed, and at the same time very effectively.

Removal of Mechanically-absorbed Water.—When wetted out, all textile fibres (whether in the loose state, as yarn, or in the piece) mechanically retain considerable quantities of water through capillary attraction. After washing and previous to drying, it is

advisable to remove the mechanically-absorbed water as completely as possible; indeed, this is imperative if the drying is to be done rapidly and economically. For, taking into account the large amount of heat which becomes latent (and is thus lost for all practical purposes) in the evaporation of the water in drying, it is at once apparent that the most efficient mechanical means for removing the water will produce the greatest economy in drying.

The mechanical removal of liquid from textile materials is principally effected in three ways, viz., by

1. Wringing.
2. Squeezing.
3. Hydro-extracting.

The following interesting account of the results of a series of comparative trials with the three methods named has been published by Grothe.* The figures given indicate in percentages (of the total absorbed) the amount of water removed in 15 minutes:—

		Wool.	Silk.	Cotton.	Linen.
For pieces.	{ Wringing,	44·5	45·4	45·3	50·3
	{ Squeezing,	60·0	71·4	60·0	73·6
	{ Hydro-extracting, . .	83·5	77·8	81·2	82·8
For yarns.	{ Wringing,	33·4	44·5	44·5	54·6
	{ Squeezing,	64·0	69·7	72·2	83·0
	{ Hydro-extracting, . .	77·8	75·5	82·3	86·0

A comparison between the effectiveness of squeezing and hydro-extracting, respectively, as a means of removing mechanically-absorbed water from cotton pieces is given by Riesler.† Six pieces of wet calico which had been through the squeezing rollers weighed 47·5 kilos. After being treated in the hydro-extractor, the same pieces weighed only 39·25 kilos. From this he calculates that for 100 pieces, 138 kilos. more water could be mechanically removed by hydro-extracting than by squeezing, which would mean for this quantity of material a saving, in the subsequent operation of drying, of 50 to 75 kilos. of coal.

1. **Wringing.**—This method is employed almost exclusively for hanks. The hanks are suspended on a rod or peg (generally fastened with one end into the wall), and twisted up tight by means of a short stick. They are then unwound, turned a quarter round and wrung or twisted again. Sometimes, as is, for instance, the case in sizing hanks, or in mordanting with oil for Turkey-red dyeing (p. 592), the wringing is done by machinery.

* *Appretur der Gewebe*, 1882, p. 616.

† Herzfeld, *Das Färben u. Bleichen d. Text. Fas.*, II., p. 288.

2. **Squeezing.**—Squeezing is employed for loose fibre, yarn, and pieces. The operation simply consists in passing the material between two rollers, one of which runs in rigid bearings, while the other (generally the upper one) is pressed against it by means of springs or weighted levers.

Squeezing rollers are employed in many of the dyeing and washing machines already described. A convenient form for yarn is that shown in Fig. 99. It consists of two india-rubber rollers geared together by spur-wheels. The pressure is exerted by spiral springs, and the machine is so constructed that it can be affixed to any dye-vat of ordinary breadth.

For the squeezing of woollen pieces in rope form, a machine is employed like that shown in Fig. 100, constructed by C. W. Tomlinson of Huddersfield. The pieces pass through the eye shown in the figure and between the squeezing rollers, which are geared together by spur-wheels, the pressure being imparted by weighted levers to the upper one. The top roller, which is plain, fits into the rut of the lower one, and the liquid is thus expressed by top as well as by lateral pressure.

3. **Hydro-extracting.**—The hydro-extractor or centrifugal ma-

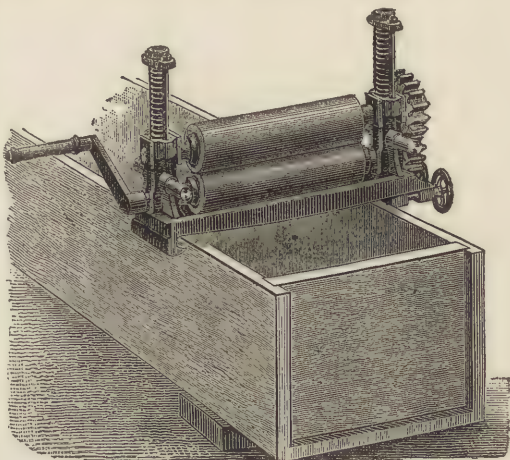


Fig. 99.—Berchtold's yarn squeezing rollers.

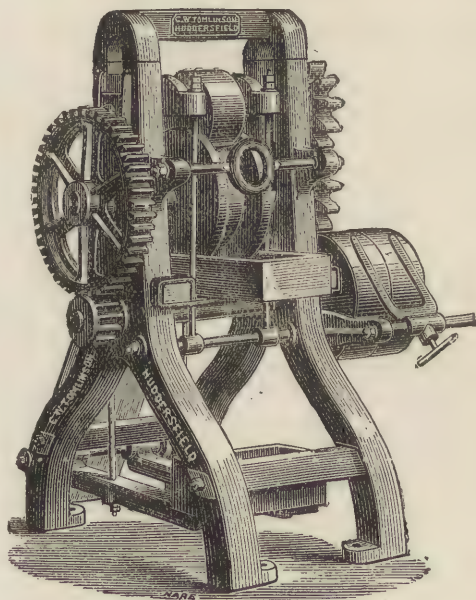


Fig. 100.—Squeezing machine for woollen pieces.

chine most in use consists essentially of a circular cage of strong galvanized iron wire or of perforated sheet copper, which is caused to revolve horizontally at a rapid rate around its centre. Any substance, the surface of which presents sufficient friction to be carried round by

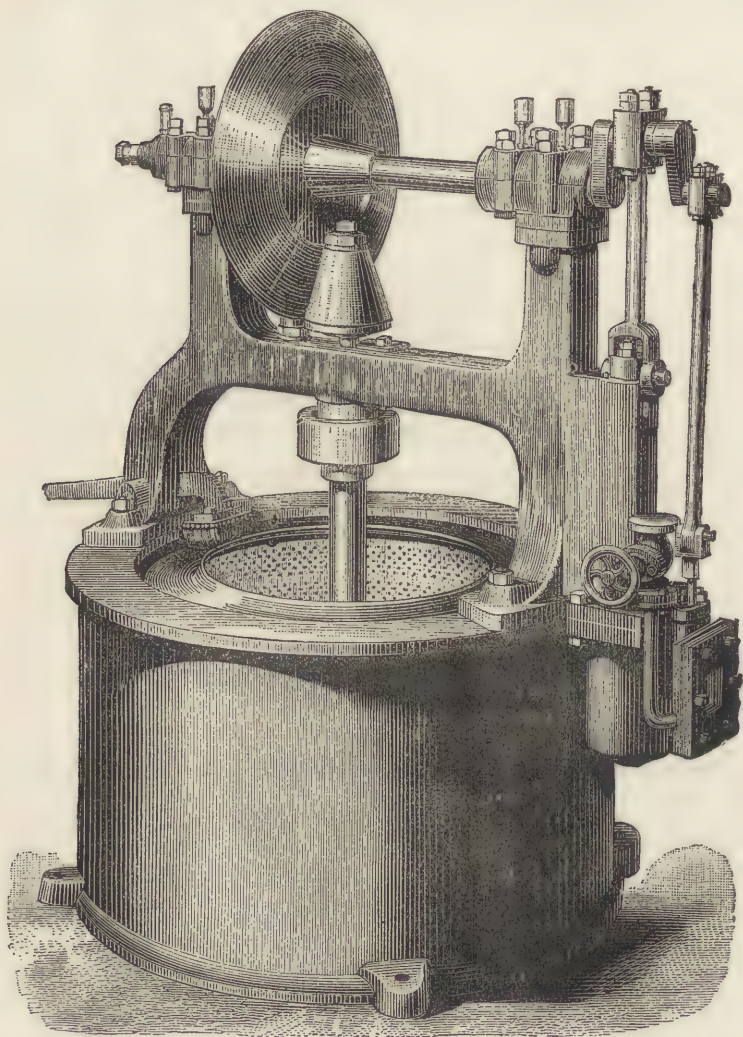


Fig. 101.—Hydro-extractor with overhead driving (Berchtold).

the cage is pressed against its periphery, and the quicker the cage revolves the greater will be the pressure exerted. If a piece of wet material is placed in a hydro-extractor and the latter is set in motion, the material is thrown by the centrifugal force against the sides of the vessel. The openings in the side of the cage being too small, the ma-

terial cannot escape, but the water which it mechanically retains, will continue to pass through the sides of the cage until the centrifugal force is equalled by the force of capillary attraction of the material. The cage is surrounded by a cast- or wrought-iron casing against the sides of which the water is thrown, whence it trickles down and flows off at the bottom.

The hydro-extractor is used for all classes of textile material, and is constructed in a great variety of forms, of which the following may be regarded as typical.

In figure 101 is shown a common form of hydro-extractor with engine attached, the driving being effected here from the top by means of bevelled friction wheels.

When the cage is unevenly balanced the hydro-extractor has a ten-

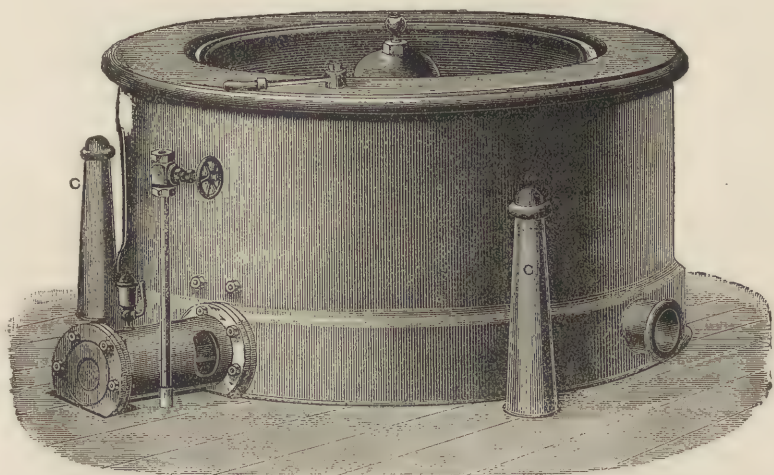


Fig. 102.—Broadbent's hydro-extractor.

dency to oscillate. To overcome this difficulty the whole machine is usually firmly fixed to a very solid foundation, and care is taken in putting the goods into the cage to lay them as evenly as possible all round. In many of the hydro-extractors of more recent construction all vibration is done away with, either by causing the cage to run in elastic bearings, or by suspending the whole machine on three columns, which are not rigid, but give slightly with the oscillatory movement of the machine. Fig. 102 shows an under-driven hydro-extractor of the latter description, with engine attached, constructed by Broadbent of Huddersfield. Two of the columns, C, on which the machine is suspended are visible in the figure.

Non-vibrating hydro-extractors working on the principle of elastic bearings (Weston's patent) are constructed by Messrs. Watson, Laidlaw & Co., of Glasgow.

Quite another form of hydro-extractor, used principally for pile fabrics and sometimes for worsteds, is that shown in Fig. 103.

It consists of a drum, D, which can be caused to revolve at a high rate of speed, and round which several pieces stitched together end to end are wound at their full breadth. The drum is surrounded by a casing, C, which is provided with a lid, L, which remains closed while the machine is working. In its action this form of hydro-extractor is

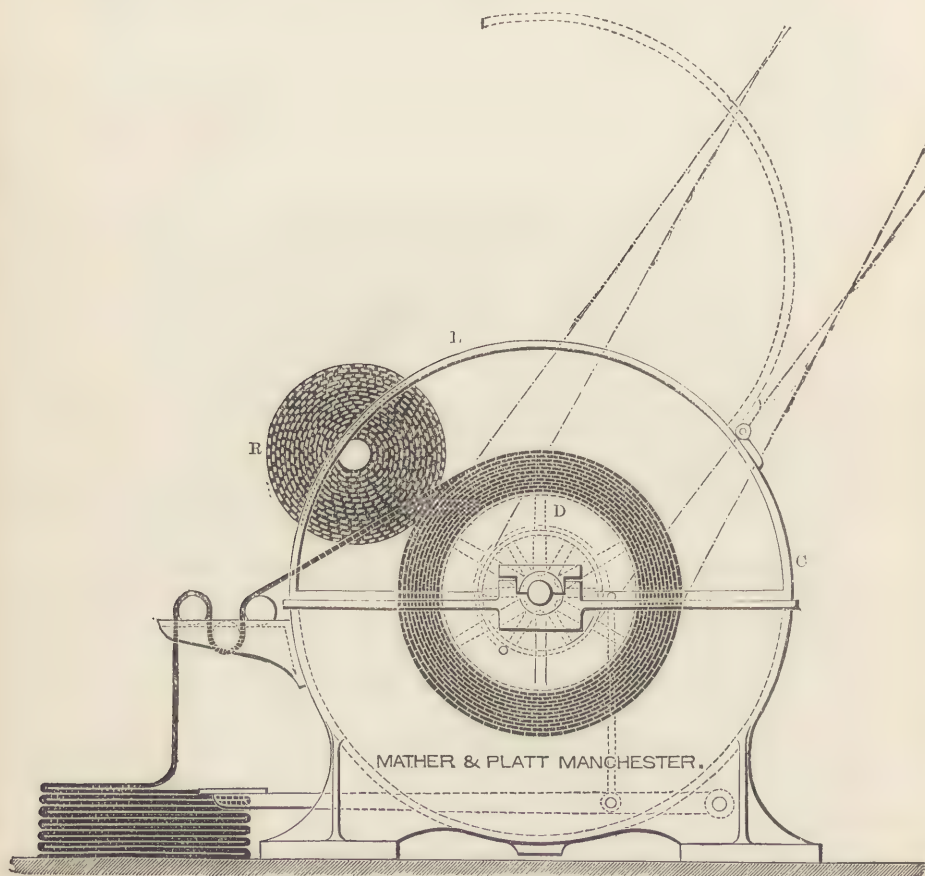


Fig. 103.—Hydro-extractor for pile fabrics.

similar to those described above, the main difference being that here the material is caused to revolve around a horizontal shaft, while in the others the shaft is vertical. After the operation is over the pieces are either drawn off and plaited down, or batched on a roller, R.

There appears to be no doubt that the hydro-extractor is the most efficient means yet devised for the removal of mechanically-absorbed water from any class of textile material. As it is, it is used largely in

dye works, especially for materials which might be damaged by squeezing rollers. But its employment would probably be considerably extended if it could be made to turn out more work in a given time than is at present the case.

Drying.—The simplest means of drying is to expose the material after it has been wrung, squeezed, or hydro-extracted, to the open air. This method of drying slowly, and at a low temperature, is certainly economical where plenty of space is available, and where time is no object; at the same time, the brilliancy of certain colours is said to be thus preserved, and the material, when dry, is in proper condition—*i.e.*, it contains about the normal amount of hygroscopic moisture.

But in the majority of works the drying is done almost exclusively by artificial means, partly because the necessary space is not available, but more especially because it is necessary to get the goods out as rapidly as possible. This is prevented in natural drying by the slowness of the process, *per se*, on the one hand, while, on the other hand, considerable delay might result from inclement weather.

Loose Fibre.—The machines employed for the drying of loose fibre call for no special description. The material, after having been squeezed or hydro-extracted, is spread out evenly on a flat surface of galvanised iron wire netting, and a current of hot air is blown through by means of fans. Machines are also constructed on the counter-current system, in which the material is carried by an endless chain through the machine, meeting on its way a current of hot air. In the machine of M'Naught (Rochdale), specially designed for the drying of loose wool, the material is fed in at one end of a large revolving cylinder, which is placed at an incline, so as to cause the wool to roll slowly to the other end. In its passage through the cylinder it meets a current of hot air, and is delivered at the other end dry.

In the Obermeier system of dyeing (p. 680) the dyed loose wool or cotton is put back into the dyeing machine, after having been hydro-extracted, and is dried by forcing a current of hot air through the machine. A similar principle is adopted in the drying of tops and cops which have been dyed by machinery.

Yarn.—Yarn in the hank is generally dried by suspending the hanks on poles in drying stoves. The stoves, through which a slow current of air is maintained, may either be heated by steam-pipes, or the air may be heated in this manner before entering. In many works, the drying stove is placed immediately above the works' boilers, and having a perforated or trellis iron floor, it receives the hot air which rises from the surface of the boilers.

Drying stoves are sometimes constructed in such a manner that the sticks or poles holding the yarn are suspended on a framework which, when filled with yarn, is run into the stove. When the yarn is dry the framework is withdrawn and the yarn taken off.

Hank-drying machines are also constructed, in which the hanks suspended on sticks are carried by two endless chains through the machine, and, meeting in their passage with a current of hot air, are delivered at the other end in a dry state. Machines of this kind act more rapidly than drying stoves, and are, perhaps, more rational than the latter; but, hitherto, they have not been introduced to any great extent into works, probably on account of the initial expense.

A hank-drying machine, by means of which the drying may be achieved at the ordinary temperature, is constructed by C. G. Haubold, jun., and is shown in Fig. 104.

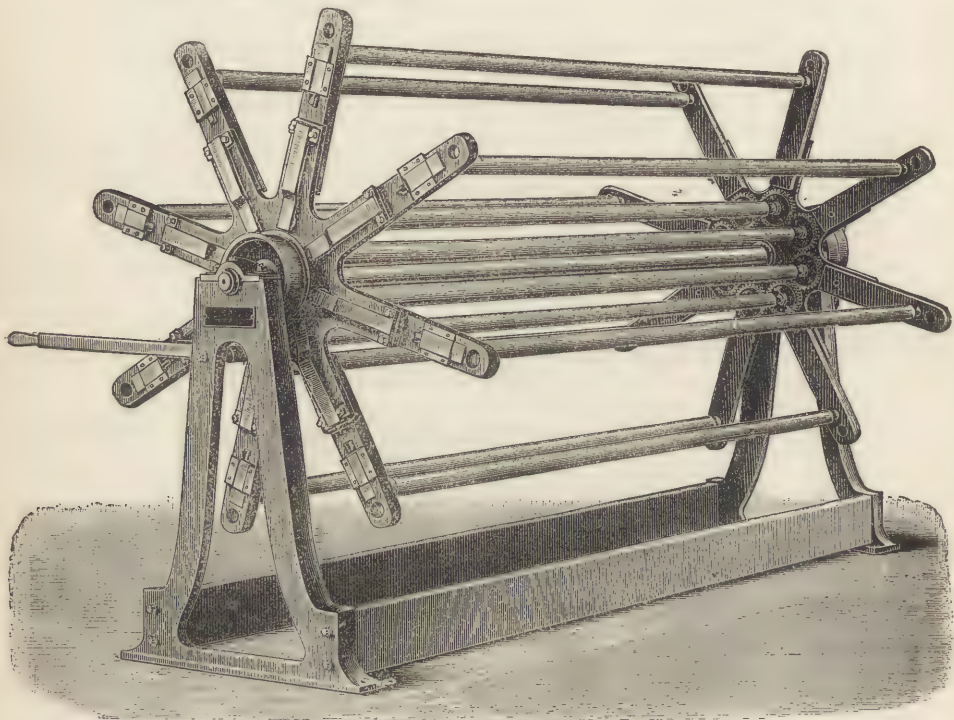


Fig. 104.—Haubold's yarn-drying machine.

The hanks are suspended from the cross-bars near the axis to those at the periphery, and the machine is set in motion. At the same time the cross-bars near the axis revolve, and the hanks are thus slowly turned as they are carried round. By means of a machine of this kind, yarn, which has been properly hydro-extracted, can be dried at the ordinary temperature in 1 to 2 hours, and has, after drying, a soft and full feel and a bright appearance.

Warps are usually dried on steam cylinders. A warp-drying machine, with two vertical sets of drying cylinders, is shown in Fig. 105.

The warps enter at the bottom, and, after passing round all the cylinders several times, are delivered dry at the top, as shown by the arrows. The cylinders, which are made of copper or tinned iron, are heated by steam.

Pieces.—Dyed pieces are almost invariably dried on steam cylinders. A horizontal piece-drying machine, consisting of eleven tinned iron or copper cylinders, geared together by spur wheels and heated by direct steam, is shown in Fig. 106.

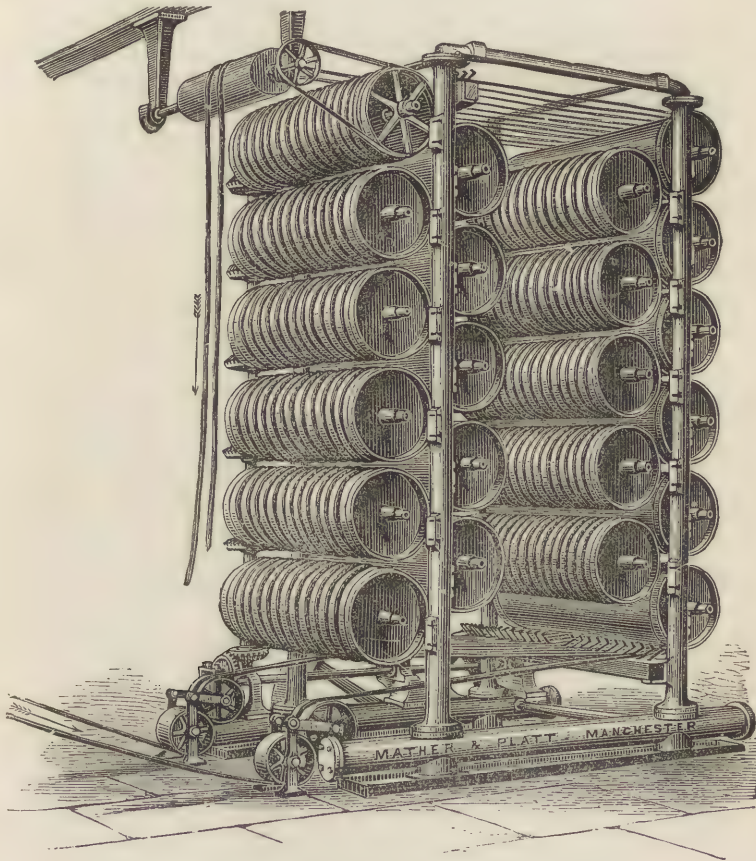


Fig. 105.—Warp-drying machine.

The course which the pieces follow in passing through the machine is distinctly shown in the figure, and requires no further explanation.

For opening out the pieces and getting out all creases before they pass on to the drying cylinders, several devices are in use. The simplest means is the so-called *scrimp-rail*, which consists of a brass-rail with incisions diverging from the centre.

An ingenious and effective arrangement for this purpose is that constructed by Messrs. Mather & Platt, and shown in Fig. 107.

Before passing on to the first drying cylinder, the pieces pass over two conical rollers, A A, on each of which a screw-thread runs from the thin to the thick end. The rollers are placed at such an angle to each other that the pieces, as they pass over them, are drawn on each side from the centre, and thus become straightened out. For

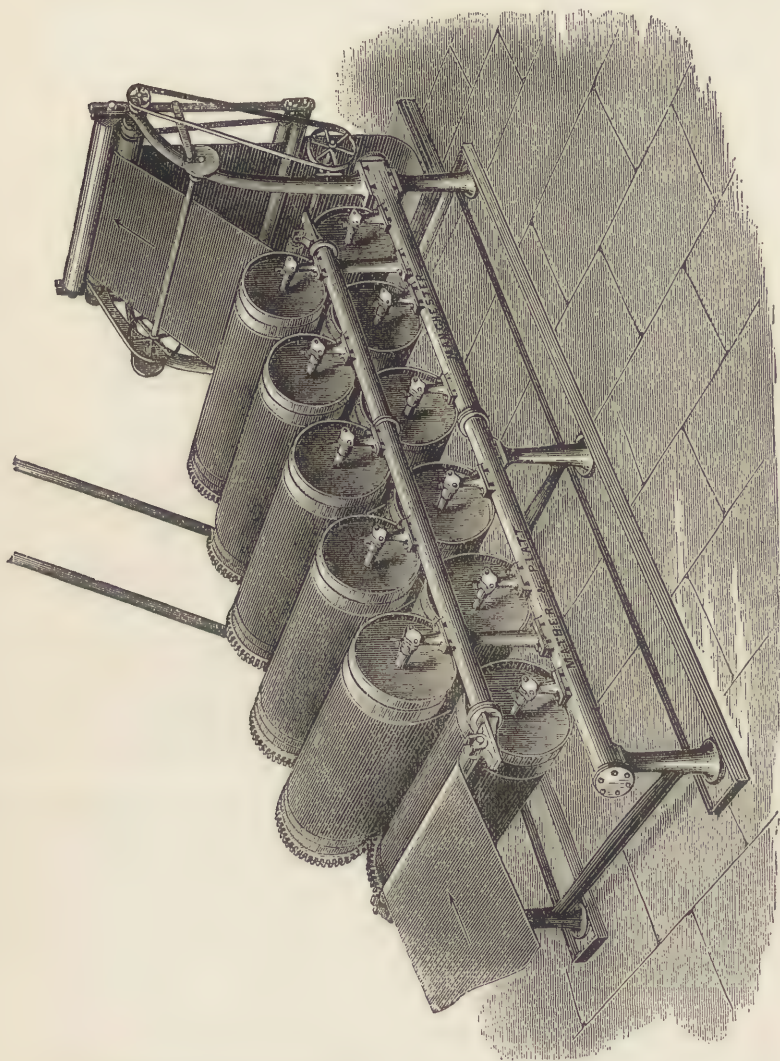


Fig. 106. — Horizontal piece-drying machine.

the purpose of keeping the pieces to the middle of the drying cylinders, the frame-work in which the rollers run is attached to the rail, R, by a swivel joint, S, which is allowed a certain amount of play. If the piece begins to run on one side, it gets on to the thick end of the expanding roller on that side, and presses the latter against an india-

rubber brake, *a*. The other roller, running free, draws the piece towards the other side, thus relieving the brake, and the pieces are in this manner not only kept straight but are forced to remain in the middle of the cylinder.

For the drying of pile-fabrics, it is essential that the pile should not be pressed against the hot surface of the cylinders, as it would thereby be damaged. Such materials are either dried in stoves or on the back only by an arrangement like that shown in Fig. 108.

After passing over the first drying cylinder, the pieces pass with

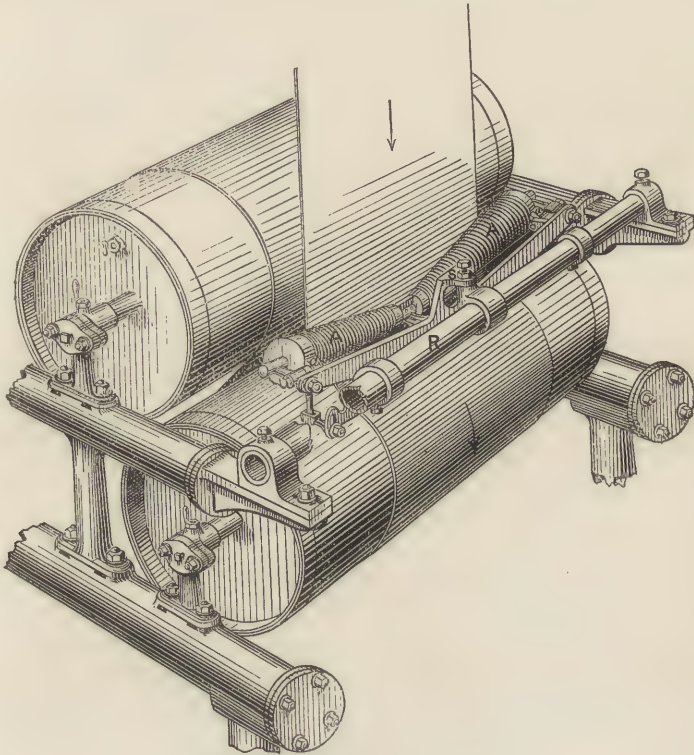


Fig. 107.—Conical opening rollers.

the face side over wooden rollers, then on to the next drying cylinder, and so on through the whole machine—always with the face away from the cylinder.

In the dyeing of pieces, the various operations through which the material has to pass almost invariably cause a certain amount of shrinkage in breadth. In order to get them to the original breadth again, they are *stretched*, *tentered*, or *stentered*. The stretching or tentering machines used for this purpose vary considerably in their construction. The principle most generally adopted is to feed the wet

or moist pieces at full breadth into the machine, where they are seized at the selvages by pins or clips borne by two endless chains which run along the whole length of the machine. The chains run in slotted frames and are not parallel, but diverge slightly from the feeding and towards the delivery end, and the pieces held by them are thus widened out to the desired degree. When they arrive at about the

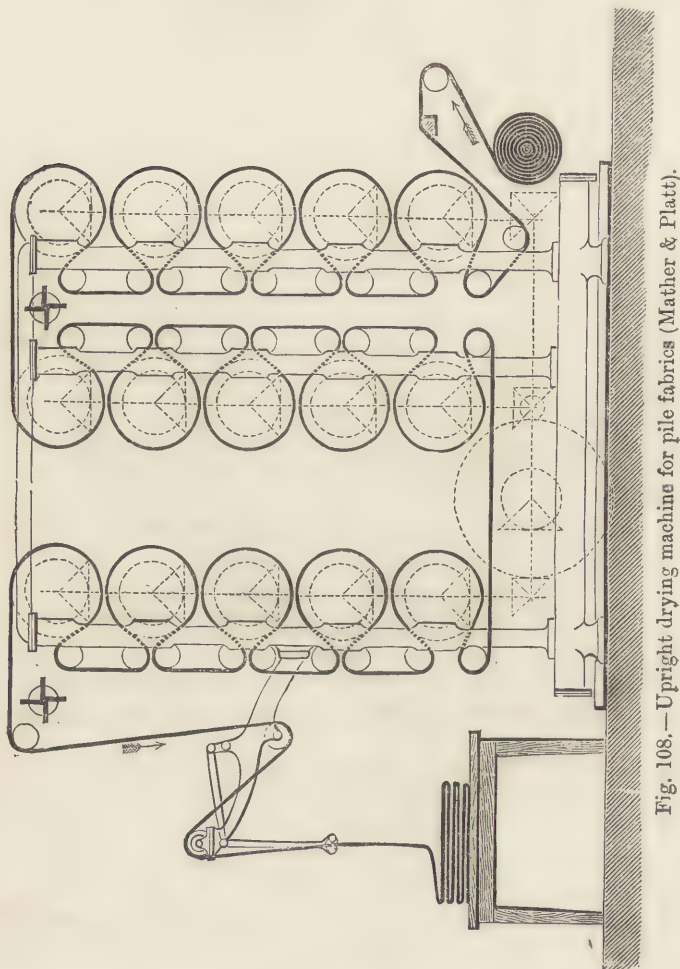


Fig. 108. — Upright drying machine for pile fabrics (Mather & Platt).

middle of the frame, heat (gas or hot air) is applied from beneath so that the pieces are dry on leaving the machine. Fig. 109 shows the appearance of a machine of this kind. The chains here carry clips, and the heating is done here by Körting's flanged steam pipes. By means of the wheel, W, the distance between the two chains may be altered to suit the width of the material to be tentered.

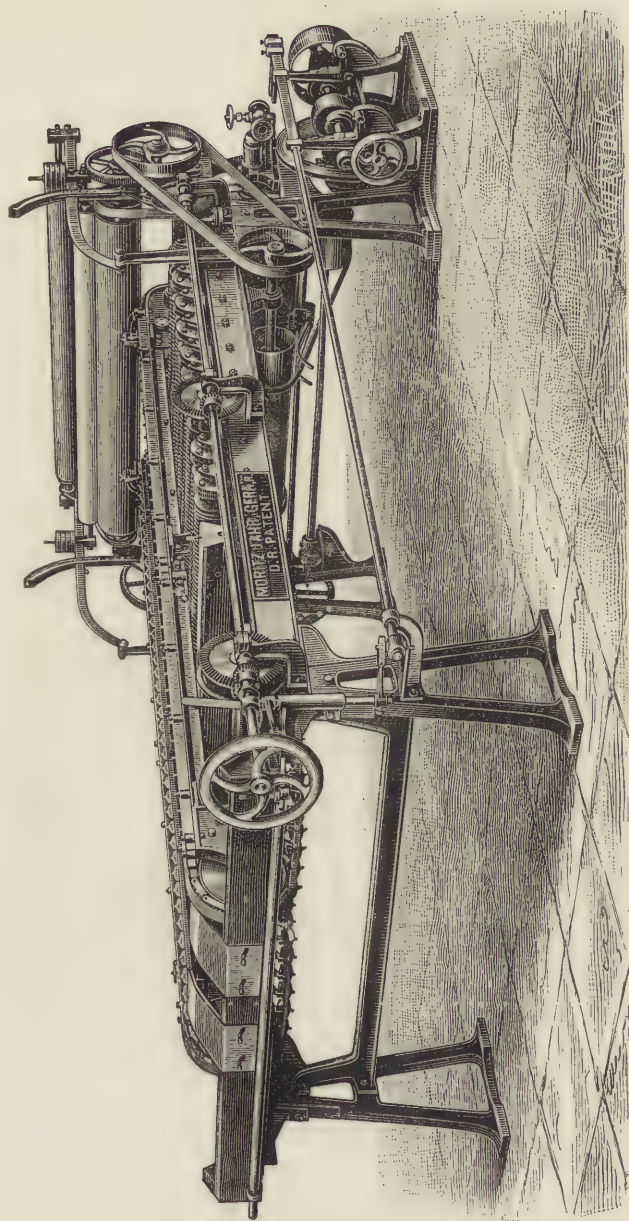


Fig. 109. — Tentering machine.

PART X.

EXPERIMENTAL DYEING.

By means of Experiments carried out on the small scale and systematically conducted, it is possible for the dyer to gain a large amount of useful information which cannot be obtained in the works, owing to the time and expense which similar experiments would involve if carried out on the large scale. Most of the new colouring matters, mordants, &c., which now come into the market are accompanied by more or less reliable recipes from the makers. But suppose, for instance, that a new colouring matter comes into the hands of a dyer with no further information than that it is a dye, he must necessarily have recourse (if he wishes to use it) to a series of experiments in order to find out whether it is more suitable for wool or for cotton, whether it requires a mordant or not, and then, having found the best mode of applying it, by more careful experiment, to determine its strength, its price, as compared with that of known dyestuffs which dye a similar shade, and its fastness to light, milling, and other agents.

Whether the colour be a *direct cotton dye* or not, is readily determined by boiling a small swatch of cotton in the aqueous solution of the dyestuff, to which a small amount of soda or soap has been added, for about 10 to 15 minutes. If a full colour remains on the cotton thus treated after washing well with water, the dye is a direct cotton dye. Such an indication would at once determine the course of subsequent experiments. If the colour is one which would be most serviceable for the production of compound shades with the other known direct dyes, it will be best to determine its strength and relative price by dyeing it on cotton by one of the methods generally employed for the direct dyes (see *Congo-red*, p. 414). But if the colour should be of such a character as to render it more useful for self-colours (as is, for instance, the case with Erika and Benzopurpurin), a series of experiments will be necessary in order to determine by comparative dye-trials the most favourable conditions as to time, temperature, concentration, additions to dye-bath, &c., for its application. The experiments might be conducted in the following order:—Three dye-trials are made with, say, fifteen, thirty, and sixty times as much

water (by weight) as material in the dye-bath (for 10 grms. of cotton, 150, 300 and 600 cc.), using say 2 per cent. of colouring matter in each case and dyeing for one hour at 100° C. in an apparatus like that described on p. 790. Cotton yarn or braid will be found most convenient for such experiments. After dyeing, the hanks are taken out, wrung, dried, and compared with each other. It will probably be found that that which has been dyed in the most concentrated liquor has the deepest colour, and this degree of concentration should therefore, strictly speaking, be adhered to in the subsequent experiments. For piece dyeing it would not be disadvantageous, but for yarns it is too concentrated for practical purposes. The one in which thirty times as much water as cotton was taken is most in accordance with practical working, and this is taken as the standard amount for subsequent experiments. Next would come experiments for the purpose of testing the effect of additions to the dye-bath, first of acids and alkalies, and then of neutral soluble salts. Of acids one might try the effect of oxalic and acetic in amounts varying from $\frac{1}{2}$ to 2 per cent. of the weight of the cotton, and of alkalies, such as sodium carbonate, potassium carbonate, sodium phosphate, borax, soap, of each 1 to 10 per cent. After having determined which alkali or acid gives the best result, and what amount is to be used, the effect of neutral soluble salts added to the dye-bath might be determined. Such salts as Glauber-salt and common salt have the effect of diminishing the solubility of most dyestuffs in water, and, in the case of direct cotton dyes, cause more to go on and into the fibre. Of common salt, the effect might be tried of say, from 2 to 100 per cent. Stannate of soda, aluminate of soda, and, more especially, Turkey-red oil and soda, frequently have the effect of producing brighter colours when added to the dye-bath; their action should, therefore, also be tried. If the water in the dyeworks is hard, a hank should be dyed in that water and compared with another dyed under similar conditions in distilled water in order to determine whether the hardness causes any loss in colouring matter in consequence of the colour forming an insoluble calcium salt. If this is the case, the water should be softened or corrected before use. The effect of temperature and time in dyeing are now soon determined, by dyeing, say, three skeins each with the same amount of dyestuff for 15, 30, and 60 minutes at the boil, and another set for one hour each cold, at 50° C. and boiling respectively. Most of the direct cotton colours do not exhaust well—*i.e.*, a considerable proportion of the dyestuff employed remains in the dye-bath, however long the dyeing may be continued. If the bath is kept and the same amount of dyestuff is added for a second lot of cotton as was used for the first, it is evident that a darker shade will result. Exhaust experiments should, therefore, be made in order to determine what amount of colour is left in the dye-bath and how much is fixed on the fibre, as well as to ascertain what quantity is necessary for obtaining the same shade on

the second and subsequent lots of material as on the first. Another important point which should not be left untried is to determine whether raw cotton, boiled cotton, or bleached cotton gives the best results in dyeing. For very light shades the employment of bleached cotton will be inevitable, but for full shades raw or boiled cotton will generally be found to give much better results.

If the colour under examination be a *basic dye*, it will dye wool, without any further addition, a full shade, but will probably only tinge the cotton. If to its aqueous solution there be added a solution of tannin and sodium acetate, an intensely coloured precipitate will result. Such a colouring matter might be suitable for both cotton and wool dyeing, but the former would have to be mordanted first by one of the known methods. Experiments might be conducted by dyeing it on cotton mordanted with different percentages of tannic acid in the first place, in order to determine what proportion of the latter is most suitable. Having obtained this result, one might try the effect of fixing the tannic acid on the cotton previous to dyeing by antimony mordants, stannous or stannic chloride, aluminium or chromium acetate, or, if dark shades are required, with an iron mordant. The effect of time, temperature, and concentration of dye-bath could be determined as in the foregoing example of the direct cotton colour.

If it is a question of an *acid dye*, the cotton will only be tinged and the wool dyed, as a rule, a somewhat meagre shade, or perhaps not at all in a neutral bath, but on the addition of a drop or two of sulphuric acid to the dye-bath, the colour will probably be rapidly absorbed by the wool and the dye-bath more or less exhausted.

Such a dyestuff is practically of no use on cotton, but may be valuable on wool. It will probably have been gathered from the preliminary experiment that no good results are obtained in a neutral bath, and a single experiment will suffice to show that the addition of only a small quantity of alkali prevents the colour from combining with the fibre. When dyed in an acid bath at the boil it will probably be seen that the colour is taken up very rapidly, and the bath is almost completely exhausted. If the colour produces a level and bright shade in this manner, and at the same time exhausts the bath, nothing further will be necessary than to determine, by comparative dye-trials, the best amount of acid to be used. But it frequently happens that the acid dyes are very prone to produce uneven or speckled effects on wool. Several methods might be tried in order to obviate this fault. In the first place, it would be advisable to try the effect of adding some such soluble salt as Glaubersalt along with the necessary acid to the dye-bath; as a rule, this has the effect of causing it to dye more slowly and more evenly. The amount employed in the comparative experiments might be made to vary from 5 to 50 per cent. of the weight of the wool. In place of sulphuric acid and Glaubersalt, the use of sodium bisulphate might be tried. Should

the colour still dye unevenly, the effect of an addition of ammonium acetate or ammonium sulphate to the dye-bath should be tried. It might be found that by boiling the wool first with a small amount of sulphuric acid (2 to 10 per cent.), or with alum and tartar, and subsequently dyeing in a neutral bath, would give better results. Further experiments might show that better results are obtained by entering the wool into the dye-bath cold, and heating gradually to the boil, or by adding the colouring matter, or the necessary amount of acid, to the dye-bath, not all at once, but in small portions at a time, or by using one of the methods indicated on p. 507. It might be that under all these conditions the dye evinced very little affinity for the wool, as is for instance the case with the indulines. In such a case it would be advisable to try the effect of chlorinating the wool before dyeing (see pp. 44 and 552).

If the colouring matter dyes neither wool nor cotton, or if it only produces very inferior shades when applied in a neutral, alkaline, or acid bath, it is probably a *mordant-dye*. Whether this is the case or not, is readily determined by boiling a piece of stripe-mordanted calico (mordanted in stripes with alumina, iron, and chromium) in the neutral dye-solution. If it was a mordant-dye, the three stripes will probably be dyed in different shades, and of these the best may be taken for further experiments. Copper and tin mordants, fixed according to methods described on pp. 288 and 295, might also be tried on cotton. Some mordant-dyes yield very poor shades on simple mordants, and if the results obtained on the stripe-mordanted calico are not good, the use of compound mordants, such as chromium and zinc (see p. 624), alumina and stannous oxide, alumina and lime, iron and lime, might be tried (see pp. 424 and 579-583). An addition of lime salts to the dye-bath in the form of calcium acetate or chalk will often be found to give beneficial results.

In place of dyeing the mordanted cotton, it might be found better to reverse the operations—*i.e.*, to pad boiled or bleached calico in the solution or decoction of the dyestuff, and afterwards develop the colour by passing through hot or cold solutions of alumina, iron, chromium, or copper salts.

In some cases the brilliancy of the dyed colour is considerably improved by steaming under pressure.

On wool, the course of experiments would be somewhat different to those conducted on cotton. By far the most important wool mordant being bichromate of potash or soda, this would be tried first. Three lots of wool mordanted respectively with bichromate of potash, with bichromate and sulphuric acid, and with bichromate and tartar would be dyed under similar conditions with equal percentages of the dyestuff and the results compared. In some cases (as for instance with gallein), very great differences in shade might be observed in this experiment. Other mordants, such as alumina, iron, copper, and tin, fixed on the

wool by the methods already described, might also be tried. Possibly better results might be obtained by stuffing and saddening—*i.e.*, by boiling the wool, first, with the colouring matter, taking of course the same percentage as used by the mordanting and dyeing method, and then developing in the boiling solution of some metallic salt, such as alum, copperas, copper sulphate, or bichromate. Possibly good results might be obtained with one or more of the different mordants by the single-bath process, as is, for instance, the case with cochineal and flavin in conjunction with a stannous salt. Should this be the case, one operation—*viz.*, that of mordanting—could be dispensed with, and if the dyestuff could be used along with others which also dye on the same mordant, a considerable saving in expense might thus be effected.

If it is intended to use the dye for silk, similar experiments to those carried out on wool could be made. If the colour dyes silk directly, the effect of alkaline boiled-off liquor on the one hand and of acidulated boiled-off liquor on the other should be tried in dyeing. After dyeing, the effect of brightening in a weak solution of tartaric acid should be tried.

In any case, a subsequent treatment of the colour dyed on the fibre, in different chemical agents, such as bichromate of potash, salts of copper, iron, &c., may bring about a useful alteration in the shade or may improve the fastness of the colour. Thus catechu is developed in bichromate, aniline-black is rendered ungreenable, and the magenta colour of chromotrop on wool is turned to a full black by this treatment. Alkali-blue dyed on wool in a neutral bath only shows its full colour after being passed through a hot dilute solution of acid. A treatment with an emulsion of oil in soap, or with a solution of neutralised Turkey-red oil, wringing and drying without washing, often has the effect of enhancing the brilliancy of colours dyed on cotton. Again, the direct cotton colours are rendered faster by treatment in boiling copper sulphate subsequent to dyeing.

After having determined by such systematic experiments the best ways of applying a colour, its fastness should be tested. Fastness to light is best tested with the colour dyed on a swatch of calico or flannel exposed to light under glass, facing the south if possible. Part of the pattern is covered up with thick cardboard, in order to protect it from the action of the light. At the same time another colour of known fastness and dyed as nearly as possible the same depth of shade on similar material, should be exposed for comparison, or rather in order to get an idea of the relative intensity of the light. The colour should be compared with the unexposed part, say after the first one or two days' exposure, and if it has not faded appreciably it might be left out for a week, a fortnight, or a month. If it has stood a month's exposure in summer without any material alteration, it may be called fast.

Fastness to washing and to bleeding or running should be deter-

mined with water alone and with soap. Yarn dyed with the colour is plaited with white yarn, and the plait boiled in water for ten minutes, wrung, dried, and the dyed yarn compared with the original in order to ascertain whether there has been any loss. It will at once be seen whether the white has remained unaffected, or whether it has been tinged, and, if so, to what extent. Although water only is used, this test is a very severe one, especially in the case of acid colours dyed on wool. In the latter case the bleeding is much more marked than if soap had been used. In a second experiment a plait made as before is worked well in a $\frac{1}{2}$ per cent. solution of neutral soap (5 grms. to the litre) for 15 minutes at 60°, and the results again compared as above. Some colours behave very differently on wool to what they do on cotton. Thus whereas, for instance, most of the direct cotton colours bleed very much when dyed on cotton, they are quite fast enough for milling on wool.

Fastness to acids may be tested in the case of the direct cotton colours by immersing the dyed material in a 5 per cent. solution of acetic acid, and observing whether there is any change in the colour. Cotton warps intended for cross dyeing should not be changed when boiled for 15 minutes in a 5 per mille solution of sulphuric acid (0.5 grm. in a litre).

Fastness to stoving is generally only required of certain colours on woollen or worsted yarns woven into white pieces to be bleached in the piece. It is tested by working the yarn in very weak soap, wringing, and exposing overnight or for 6 to 8 hours to an atmosphere of sulphurous acid. If in the works, it is best to expose in an ordinary sulphur stove, but if this is not convenient, the yarns may be suspended in a wooden box into which a slow current of sulphurous acid gas is passed from a syphon, or from some apparatus evolving the gas.

Fastness to chlorine may be tested by steeping the cotton yarns after boiling in alkali, for an hour in weak bleaching powder solution ($\frac{1}{4}$ ° to $\frac{1}{2}$ ° Tw.), washing well in water, then passing through dilute sulphuric acid (1° Tw.), washing again, and drying.

FAST AND LOOSE COLOURS.

The term *fast*, as applied to the colour of dyed materials, usually implies, in the first place, that the colour will withstand the action of *light*, and, in the second place, that of *washing*. Fastness to light and washing are the principal, but not the only, desiderata of a good colour.

Fastness to *acids* is also frequently required, especially in cotton warps intended for cross dyeing, in wools which are carbonised after dyeing, and in dyed materials which are worn next to the skin, and which should not be affected by the organic acids contained in the

perspiration. In large towns where much coal is burnt, and in rooms in which gas is used, the atmosphere usually contains sulphurous and sulphuric acids in small quantities, and these are liable to act injuriously on certain colours, the former in consequence of its acid and reducing properties, the latter by its acid properties only.

A further desideratum in a good colour is fastness to *rubbing*, by which is meant that the dyed material, when rubbed on a piece of rough white paper or linen, should not colour it. Most colours either do not rub, or can easily be deprived of this property by washing with soap. The defect is most marked, and also very difficult to remove, in the case of the two important colours, indigo and aniline-black.

Some colours possess the drawback of volatilising from the fibre on which they are dyed at the ordinary temperature of the atmosphere, and are, therefore, totally unsuitable as dyestuffs. A still larger number are partially volatilised in *steaming* or *hot-pressing*, and their employment in printing and in piece goods which are hot-pressed in the process of finishing should, therefore, be carefully avoided.

Fastness to *stoving*—i.e., to the action of sulphurous acid—is required principally for yarn-dyed wool which is woven into white piece goods (such as blankets), which are subsequently bleached in the piece.

Fastness to *chlorine*, or rather to weak bleaching-powder solution, is required of yarn used, for instance, as headings in towels or other fabrics with coloured stripes which are bleached in the piece.

The mud which collects in the streets of towns in wet or moist weather is known to have a destructive action on certain colours in ladies' dress-goods. To what this is actually due does not seem to have been definitely ascertained, but it is generally supposed to be due to limestone or to an alkaline action of the mud caused by the presence of decomposing nitrogenous matter.

Besides these destructive influences, to which dyed goods may be exposed in the ordinary course of things, there are others of minor importance to which the dyer is now and then desired to dye fast shades. The action of light and of washing on dyed colours by far outweigh in importance the action of other agencies; they will, therefore, be considered in the following account.

Action of Light on Dyed Colours.—None can have failed to observe that some colours fade more or less rapidly when exposed to light, whereas others undergo no appreciable change. The former are designated *fugitive*, the latter *fast* colours; but between these there are many intermediate degrees. In the description of the properties of the colouring matters we have classified them in four degrees of fastness—viz., *fast*, *fairly fast*, *moderately fast*, and *not fast*.

As *fast* are to be regarded such colours as indigo (on wool), Turkey-red, anthracene-brown (on chromium mordant), aniline-black, tartrazin, &c., which do not lose appreciably after, say, a month's exposure to direct sunlight in summer.

As *fairly fast*, such colouring matters are classed which, like methylene-blue (on cotton), crocein-scarlet (on wool), soluble blue (with tin mordant on cotton), fustic (on chromium mordant), cochineal (on tin mordant), and some of the red, orange, and yellow azo-dyes, lose an appreciable amount of colour during the same time of exposure.

The designation *moderately fast* has been applied to those colours which, like the majority of the red, orange, and yellow azo-dyes on wool, several of the direct cotton colours, &c., are in medium shades strongly affected by two weeks' exposure to direct sunlight.

Not fast are those colours which, like the majority of the direct cotton colours and basic colours, show a marked change after a few days' exposure and are more or less bleached or altered in shade after a month's exposure.

It is difficult to give here a more exact classification, as the authors have not had an opportunity of comparing the whole range of natural and artificial colouring matters simultaneously and under exactly the same conditions. Only in this manner can a more accurate comparison be made. That published statements regarding the fastness to light of colouring matters vary considerably is not to be wondered at when we consider how enormously the conditions of exposure may vary with different observers. One may expose his patterns in the open air to the joint action of sunlight, wind, rain, and, possibly, frost; another may expose under glass and place the patterns so as to get the largest possible proportion of the direct rays of the sun, or he may perhaps expose in diffused daylight only. Again, the climate, the weather, the time of the year, are all important factors which must necessarily be taken into account if anything like an accurate result is to be arrived at. With the possibility of such varying conditions, it will be easily understood how one observer may obtain a result which leads him to infer that a colour is not fast, whereas another, who may have exposed the same colour for the same length of time, concludes that the colour is fast. It is to be regretted that we have no recognised standard for the testing of colours as to their fastness to light, and much credit would be due to anyone who would take the trouble to work this out. It would undoubtedly be a step in the right direction if, when exposing to direct sunlight under glass, we could agree as to which position the board on which the patterns are fixed should be placed in, and in giving the result, mention the number of hours of direct sunlight (measured by the heliograph) and of diffused light to which the patterns have been exposed. By a series of experiments the ratio of the destructive action of direct sunlight and the average of diffused daylight could possibly be determined, and we should thus be enabled to express the duration of exposure in one term—viz., hours of direct sunlight. If this were done, there would be much less divergency of opinion regarding the fastness to light of colours. For exact

measurements, however, it would be necessary to measure the average intensity of the sun's rays during the different seasons of the year and for different climates.

An important factor in judging of the fastness to light of colours, and one which is not often taken into account, is the condition of the atmosphere. It has been observed that dyed colours exposed in large towns, or in their vicinity, show unmistakable evidence of the presence of acids in the air, while the air of the country has an alkaline reaction. It does not seem to have been ascertained exactly to what extent this affects the actual fading of the colours, but the fact is nevertheless sufficiently noteworthy to be taken into account.

Direct sunlight acts the most powerfully on dyed colours, diffused daylight is much less destructive. Of artificial lights, the electric arc-light resembles sunlight in its action, but it is not so powerful.* In exposing colours dyed on wool under glass to the action of an electric arc-light (possessing an illuminating power of 200 gas-flames) at a distance of 1.5 metre, for 1,500 hours, the action was found to be about one-fourth of that of sunlight. Differently-coloured lights act differently on dyed materials. Dépierre and Clouet† studied the effect of white sunlight, electric light, and coloured lights corresponding to the following colours on Chevreul's colour-scale :—

Red	2 R
Orange	4 O
Yellow	G b
Yellowish-green	4 Gr B
Blue	2 B
Violet	1 B

on 76 typical colouring matters (natural and artificial) printed on calico.

The following is a summary of the decolorising action of the different lights :—

	Units decolorised.
White sunlight,	2256 in 7600.
Blue " 	1265 "
Yellow " 	1255 "
Green " 	968 "
Orange " 	856 "
Violet " 	713 "
Red " 	533 "
White electric light,	404 "

The following scheme shows the action of the different-coloured rays on the different colours :—

Strongest action.	Least action.	On material dyed.
Yellow rays.	Red rays.	Red.
Blue "	"	Orange.
Blue "	"	Yellow.
Blue "	"	Green.
Yellow "	"	Blue.
Blue "	"	Violet.

* Décaux, *Journ. Soc. Dyers and Col.*, 1885, p. 247.

† *Journ. Soc. Dyers and Col.*, 1885, p. 245.

The coloured lights experimented with do not of course represent the corresponding parts of the spectrum, and will all contain more or less white light. It is probable that the violet and ultra-violet rays, which are known to possess the greatest chemical action, also have the strongest bleaching action.

No satisfactory theoretical explanation has hitherto been given of the bleaching action of light. It is probable that light alone cannot bring about such changes. Chevreul exposed several dyed patterns to light in exhausted glass tubes and in tubes filled with indifferent gases, and found that under these circumstances several otherwise very fugitive colours were either unaffected or very much less affected than when exposed under ordinary conditions. The yellow colour of raw cotton withstands well the action of light, but after boiling with alkalis, it is soon bleached in direct sunlight. Whether this fact is due to chemical changes brought about by the alkali, or to the removal of the thin covering of cotton wax has not yet been ascertained, but it is probably due to the latter cause. According to Franc,* dyed colours may be rendered fast to light by impregnating the dyed materials with a solution of linseed oil in naphtha and drying. The direct cotton colours are rendered faster to light by a treatment in boiling copper sulphate solution. According to Scheurer† the protective influence of the copper salt is not due, as was at first supposed, to the formation of a lake, but to the fixation of a certain amount of the copper salt in the fibre, which does not permit the chemical rays to pass.

The theory of the bleaching action of light at present most generally accepted, is that the light causes oxidation and the colours are thereby destroyed. When water evaporates, ozone and peroxide of hydrogen—both powerful oxidising agents—are produced in small quantities, and since, owing to their hygroscopic properties, evaporation or absorption of moisture must always be going on in the textile fibres, with changes in the temperature and the hygrometric condition of the atmosphere, these reactions are regarded as being the principal cause of bleaching.

The fastness of a colour to light will depend to a very great extent on the mode of fixation, but principally on the mordant employed. Thus, fustic dyed on wool on a tin mordant gives a yellow which is not at all fast to light, but with a chromium mordant (bichromate) the yellow obtained with the same colouring matter may be classed as fairly fast. Logwood on chromium mordant is not as fast as when dyed on copper mordant. Alizarin-blue fixed with zinc gives a fine blue, but the colour thus produced cannot compare in fastness with alizarin-blue fixed on chromium. A great difference is observed with the basic coal-tar colours fixed on Turkey-red oil, on tannic acid, and on tannic acid and tartar emetic respectively. On the oil mordant they are all extremely fugitive, whereas on the tannin and tartar

* *Journ. Soc. Dyers and Col.*, 1886, p. 94.

† *Ibid.*, 1889, p. 44.

emetic some may be classed as moderately fast. Tannic acid alone holds, as a fixing agent, an intermediate position.

On the other hand, the fastness of a colour will depend in certain cases on the nature of the fibre on which it is dyed. Thus, indigo is not nearly so fast to light on cotton as on wool, whereas methylene-blue dyed on cotton with tannin and tartar emetic mordant is much faster than on wool.

Fastness to Washing.—With certain classes of dyed and printed materials, fastness to washing is of prime importance, whereas with others it is not of much moment. Thus printed calicoes which have to be frequently washed (often by boiling with soap and soda), and the colours in figured woollen goods which are milled with soap during the process of manufacture, must necessarily be fast to washing. On the other hand, in such goods as carpets, furniture coverings, and fine silks this fastness is not necessary.

The behaviour of colours in washing varies enormously. Some, like the ordinary azo-scarlets and oranges fixed on cotton are stripped by water alone. The direct cotton colours dyed on cotton mostly give up a certain amount of colour to boiling water, but only up to a certain point and no more can be removed unless fresh water be used. Most colours are little affected by boiling water, but are easily affected by soap, especially by such as contains free alkali. Some colours, lastly, like aniline-black, indigo, and most of the alizarin colours fixed on chromium mordant are fast enough to withstand the action of hot soap. Since the production of shades fast to washing generally involves a larger number of operations, the use of more costly dyestuffs, and, consequently, greater expense to the dyer, he will, as a rule, employ those dyestuffs and methods which will bring about the desired result in the least time and at the smallest cost, and will only produce fast shades where they are a requirement of the trade or when specially asked for.

The loss of colour in washing is not the only drawback which the dyer has to guard against, especially in dyed yarns which are used in figured fabrics. Many colours have the disagreeable property, when partially stripped from the fibre, of colouring other yarns in the piece, especially the whites. Such colours are said to "bleed" or "run," and their use in any fabrics which have to stand washing, other than plain ones, must be carefully avoided.

PART XI.

ANALYSIS AND VALUATION OF MATERIALS USED IN
DYEING.

IN this division we shall treat of the various processes employed for the analysis and valuation of dyes, mordants, and other substances used in the dye-house.

Not very many years ago it was quite the exception to find a dyer troubling himself about any examination of the dyes, &c., which he used; but the importance of attending to this matter is gradually becoming recognised. In many of the larger dye-works chemists are now daily engaged testing the various materials used. The expense incurred by analysis is very small in comparison with the saving thereby often effected. It is, of course, of the greatest importance that care be taken with the analyses, and that the methods employed be capable of giving accurate results. The methods given in the following pages have been carefully selected, and, unless otherwise stated in the text, are known from our own practical experience to be trustworthy and reliable. As will be fully described later on, the majority of dyes should be examined by means of comparative dye-tests; but it is important to bear in mind that, to be of any value, these dye-tests demand as much care and attention as a chemical analysis. Whenever possible, however, a chemical examination is to be preferred.

The methods employed in quantitative chemical analysis may be broadly divided into two classes—viz., *gravimetric* and *volumetric*. In order to determine the amount of a given constituent of a substance by gravimetric analysis, it must either be separated in a pure state, or be converted into a compound of a known and definite composition, purified and weighed. In volumetric analysis the amount of the required body is determined by means of so-called standard solutions—i.e., solutions of a known strength. From the volume of the standard solution required to effect a certain result the weight of the body to be estimated is determined. In a great number of cases no separation whatever is required, the substance being estimated in the presence of several other bodies which have no effect upon the reaction involved. A necessary condition of volumetric analysis is that the

end of the operation must be unmistakable to the eye. In the great majority of cases a substance termed an *indicator* is used, which shows, either by a change in colour, or by the formation or disappearance of colour, when the operation is complete. The indicator is sometimes added to the solution under examination, whilst in other cases a drop of the solution is brought from time to time into contact with the indicator outside the liquid. Since volumetric processes are much more rapidly performed than gravimetric, they are, when practicable, almost invariably used in technical analysis. In some cases, however, where no suitable volumetric process is applicable, recourse must be had to gravimetric analysis.

NORMAL SOLUTIONS.

Some difference of opinion has existed among chemists regarding the significance of normal solutions used in volumetric analysis. Most chemists, however, at the present day are agreed that normal solutions (as described by Sutton) are such that contain in one litre the hydrogen equivalent of the active reagent in grammes. In other words, a litre of a normal solution of any substance is of such a strength that it will exactly neutralise, replace, or oxidise 1 gramme of hydrogen or its equivalent. Normal solutions are, therefore, based upon equivalent weights—not *atomic weights*. The following table shows a few examples of normal solutions:—

Potassium hydrate, . . .	56	grammes	K H O	per litre.
Ammonium „ . . .	17	„	N H ₃	„
Sodium carbonate, . . .	53	„	Na ₂ C O ₃	„
Hydrochloric acid, . . .	36.5	„	H Cl	„
Sulphuric acid, . . .	49	„	H ₂ S O ₄	„
Nitric acid, . . .	63	„	H N O ₃	„
Sodium chloride, . . .	58.5	„	Na Cl	„
Silver nitrate, . . .	170	„	Ag N O ₃	„
Oxalic acid, . . .	63	„	C ₂ H ₂ O ₄ , 2H ₂ O	„
Potassium permanganate, .	31.6	„	K Mn O ₄	„

A given volume of any of the above *alkaline* solutions will exactly neutralise the same volume of any of the *acid* solutions and *vice versa*. A given volume of the sodium chloride solution will exactly precipitate the silver in the same volume of silver nitrate solution. And again the potassium permanganate solution will completely oxidise exactly the same volume of oxalic acid. It will be observed that in the case of dibasic acids, one half of the molecular weight in grammes forms the normal solutions. Also that one-fifth of the molecular weight of potassium permanganate is taken, since one part of this salt is capable of oxidising five parts of hydrogen. The advantages of having solutions made up on this principle are manifold. If, for example, it is required to know the amount of carbonate of soda in a

sample of refined soda ash, the number of cubic centimetres of any normal acid required to neutralise 5.3 grammes of the sample expresses the percentage. If 3.1 grammes of the sample were taken, the number of cubic centimetres (cc.) of any acid required would correspond to the percentage of sodium oxide present. In like manner, by titrating 4.7 grammes of a sample of caustic potash or potassium carbonate with a normal acid, the number of cc. required to effect neutralisation gives the percentage of potassium oxide (K_2O) present. By varying the amount of substance weighed out in the proportion of equivalent weights, the use of normal solutions enables the percentage of the body sought to be directly expressed. In many cases it is found in practice more convenient to employ weaker solutions than those above mentioned. For such purposes seminormal, quintinormal, decinormal, and centinormal solutions (indicating solutions one-half, one-fifth, one-tenth, and one-hundredth as strong as normal solutions) are frequently used and are usually abbreviated $\frac{N}{2}$, $\frac{N}{5}$, $\frac{N}{10}$, and $\frac{N}{100}$ respectively. In certain technical analyses where a standard solution is used for the determination of one substance only, it may be found more simple and advantageous to employ an empirical standard solution of such a strength that every cubic centimetre shall represent either one decigramme, centigramme, or milligramme of the body to be estimated. For example, supposing a number of analyses of refined alkali (sodium carbonate) are constantly being made for sodium oxide only. A standard acid might be prepared, so that each cubic centimetre neutralised 0.01 grm. Na_2O , when the number of cubic centimetres required to neutralise 1 gramme of the sample would directly express the percentage.

For fuller particulars regarding the principles of volumetric analysis, works such as Sutton's should be consulted.

Alkalimetry and Acidimetry.—These are terms used denoting the methods employed for determining the amount of alkali and acid respectively in various substances. Alkaline bodies are determined by standard solutions of acids and, *vice versa*, acids by standard solutions of alkalies.

Indicators.—The exact point of saturation is shown by an indicator. The principal indicators used in alkalimetry and acidimetry are methyl-orange, phenolphthalein, lackmoid, cochineal, and litmus. Numerous others have been recommended, but, except perhaps in special cases, they possess no advantages over those enumerated. It must not be supposed that in all cases any one of these indicators is applicable. Although with the stronger mineral acids in conjunction with caustic alkalies all the indicators show the same neutral point, *i.e.*, when the acid and alkali have combined in such proportions as to form a normal alkaline salt, there are numerous cases where one indicator shows a neutral reaction with a normal salt and another indicator a neutral reaction with an acid salt of the same base. Sodium

sulphite ($\text{Na}_2\text{S O}_3$), for example, is neutral to phenolphthalein, and alkaline to methyl-orange, whereas sodium bisulphite (Na H S O_3) is neutral to methyl-orange and acid to phenolphthalein. There are other cases again where certain indicators are unsuitable on account of a want of precision and sharpness in the end reaction. Phenolphthalein, for example, is unsuitable for titrations with ammonia, and litmus is indefinite with acetic, citric, and other organic acids, as well as in the presence of carbonic acid. The characteristics of indicators have been carefully studied by R. T. Thomson.*

Methyl-orange.—This solution may be prepared by dissolving 1 gramme of the colouring matter in a litre of water; 2 or 3 drops of which will be sufficient for each titration. An alkaline solution is of a very pale-yellow colour, but with the slightest excess of acid a pink colouration is developed. It is unaffected by carbonic acid and sulphuretted hydrogen. Carbonates can, therefore, be titrated in the cold.

Lackmoid is prepared by the action of sodium nitrite on resorcin. 1 grm. of the colouring matter is dissolved in 100 cc. of a mixture of equal parts alcohol and water. Alkaline solutions are blue, and acid solutions red; the change being sharp and well defined. Its properties as an indicator are similar to methyl-orange. Paper prepared with lackmoid has many advantages over the solution. Lackmoid paper admits of the determination of carbonates and bicarbonates with more precision than the solution. The paper is also of great service in the case of highly-coloured solutions, and in titrating chromates and chromic acid, *bichromates* being exactly neutral to lackmoid.

Cochineal.—A solution is prepared by heating 5 grms. of ground cochineal with 500 cc. of 20 per cent. alcohol, and filtering from the insoluble matter. Its natural colour is orange, which is turned violet by alkalis. It is not appreciably affected by carbonic acid. It is useful in the titrations of alkaline earths and soaps, although it cannot be said to have any distinct advantage over methyl-orange.

Phenolphthalein is a most useful indicator. One gramme of the substance is dissolved in 100 cc. of 90 per cent. alcohol. The liquid is colourless in neutral and acid solutions, but the faintest excess of alkali gives an intense red colour. Two or three drops are sufficient for each titration. It is especially serviceable in the estimation of acids with standard solutions of caustic potash or soda. It is not available for ammonia, nor for the estimation of carbonates, unless the liquid is well boiled so as to completely expel all carbonic acid. For many weak organic acids it is the only indicator which gives good results. It is also exceedingly useful in the estimation of free caustic alkali in such substances as soap, as well as for free fatty acids in oils, and determination of saponification equivalents of oils, &c., &c.

* *Chemical News*, vol. 47, pp. 123, 135, 184; vol. 49, pp. 32, 38, 119; vol. 52, pp. 18, 29.

Litmus.—About 10 grammes of solid litmus are ground and treated with 80 per cent. alcohol to remove certain colouring matters not affected by acids and alkalies. The residue is repeatedly treated with cold water, and the solution obtained acidulated with sulphuric acid and boiled. Barium hydrate is now cautiously added to precipitate the sulphuric acid, and the baryta in its turn precipitated by carbonic acid. The liquid is filtered and made up to half a litre. It should be kept in a bottle to which air has free access. Litmus is not serviceable in the presence of free carbonic acid, and it gives no definite end-reaction with most of the organic acids. With mineral acids and caustic alkalies, litmus, like other indicators, is sharp and delicate, but it possesses no advantages over methyl-orange. With the two indicators, methyl-orange and phenolphthalein, practically all acidimetric and alkalimetric operations can be performed, and most chemists have now discarded litmus altogether.

Preparation of Standard Solutions:—

Normal Sulphuric Acid.

1 litre = 49 grammes H_2SO_4 .

About 30 cc. of pure concentrated sulphuric acid (preferably distilled) are diluted with four or five times as much water, the mixture allowed to cool, and then made up with more water to a litre. This solution will now require standardising—that is, its strength must be accurately ascertained. For this purpose 1.06 grms. of pure anhydrous sodium carbonate are dissolved in about 100 cc. of water and a few drops of methyl-orange added. The sulphuric acid solution is now run in from a burette until a faint pink colour is produced. The operation is best performed in a white porcelain dish, stirring the liquid with a glass-rod whilst the acid is being run in. If the acid were strictly normal, exactly 20 cc. would be required, but in all probability it will be found too strong. Suppose 19.5 cc. of the acid solution were required, it is evident that this amount contains as much sulphuric acid as 20 cc. of strictly normal acid. Consequently, in order to make the acid of the required strength, all that is necessary is to accurately measure the volume of solution and add water in the proportion of .5 cc. to every 19.5 cc. Another titration with 1.06 grms. of pure sodium carbonate is now made, when, if care has been duly taken, exactly 20 cc. of the acid will be required. One standard acid at least should be prepared with the greatest care, leaving no doubt of its accuracy. As sulphuric acid can be very accurately estimated gravimetrically by means of barium chloride, the volumetric determination may be controlled in this way. It is important to bear in mind that the sulphuric acid used should be free from sulphates, otherwise the precipitation method would give too high results. The acid on ignition should leave no appreciable residue, neither should it contain ammonium sulphate. In order to control

the strength of normal sulphuric acid gravimetrically, 10 cc. may be withdrawn by means of an accurate pipette, and diluted with about 150 cc. of water. A few drops of hydrochloric acid are added, and the liquid heated to the boiling point, when a solution of barium chloride is slowly and carefully added until no further precipitate takes place. The solution is now kept hot for two or three hours on the water bath (the beaker being covered with a clock glass to prevent evaporation), after which time the clear liquid is poured on a filter, and the precipitate treated with boiling water. The barium sulphate is thus washed two or three times by decantation, when it is wholly transferred to the filter and washed with hot water until free from either barium or chlorine, shown respectively by adding sulphuric acid or silver nitrate to a little of the filtrate. The filter and contents are dried, the precipitate transferred to a weighed crucible, the paper incinerated separately and added to the bulk, and the whole heated at first gently, and then to bright redness for 10 minutes, cooled, and weighed. 10 cc. of normal sulphuric acid treated in this manner should give 1.165 grms. of BaSO_4 , corresponding to 0.490 gm. of sulphuric acid. From the normal sulphuric acid, $\frac{N}{2}$, $\frac{N}{5}$, and $\frac{N}{10}$ solutions may be prepared by carefully diluting with the requisite amount of distilled water.

Normal Hydrochloric Acid.

1 Litre = 36.5 grammes of HCl .

Hydrochloric acid boiling under the ordinary atmospheric pressure has a constant composition. It contains 20.2 per cent. HCl , and has a specific gravity of 1.10. If 181 grms. or 164.5 cc. of this acid be diluted to a litre it forms an approximately normal solution, which may be standardised volumetrically exactly in the same manner as sulphuric acid, 1.06 grms. of pure sodium carbonate requiring 20 cc. of the normal acid as with sulphuric.

Normal Caustic Soda.

1 Litre = 40 grammes of NaOH .

About 50 grms. of pure caustic soda of commerce (purified by alcohol) are dissolved in a litre of water and the solution (25 cc. or 50 cc.) titrated with normal sulphuric acid and methyl-orange. The solution will most probably be found too strong. It is carefully diluted with the requisite amount of water (as in the adjustment of sulphuric acid described above), and again titrated when 25 cc. should be exactly neutralised by 25 cc. of the normal acid.

ANALYSIS OF ALKALIES AND ACIDS.

Analysis of Sodium Carbonate.—Sodium carbonate, in a state of greater or lesser purity is known in commerce under such names as

soda ash, refined alkali, crystal carbonate, soda crystals, &c. Soda ash varies greatly in composition; some qualities consisting almost entirely of sodium carbonate, whilst others contain more or less caustic soda, as well as many impurities—sulphides, sulphites, sulphates, iron, calcium, alumina, &c.

In some cases it may only be necessary to determine the amount of total alkali present; in others the caustic soda as well as the carbonate; whilst in others again a more complete analysis may be required.

Insoluble Matter.—10 grms. of the sample are dissolved in hot water, filtered, and the residue washed until free from soluble salts. The filter and residue are then dried and ignited in a crucible and weighed.

Total Alkali.—The filtrate and washings are cooled and diluted to a litre; 100 cc. are withdrawn by means of a pipette, and, with methyl-orange as an indicator, titrated with normal sulphuric acid. Each cc. of acid required corresponds to .031 gm. Na_2O or .053 gm. Na_2CO_3 .

Caustic Soda.—250 cc. of the solution (10 grms. per litre) are put into a 500 cc. flask, an excess of a perfectly neutral solution of barium chloride added, and the flask filled to the mark with distilled water which has been recently boiled and cooled so as to be free from carbonic acid. The flask is well shaken and then allowed to remain at rest until the precipitated barium carbonate has subsided, when 200 cc. of the clear supernatant liquid (equal to 100 cc. of original solution) are withdrawn and titrated with $\frac{N}{10}$ sulphuric acid. Either methyl-orange or phenolphthalein may be used in this case as indicator. Each cc. of $\frac{N}{10}$ acid corresponds to .0031 gm. Na_2O or .004 gm. NaOH .

If oxalic acid is used in place of sulphuric or nitric acid, the titration may be carried out in the liquid containing the precipitated barium carbonate, and the time allowed for settling is thus saved.

Caustic soda may also be determined in a *caustic soda ash* by means of strong alcohol, sodium carbonate being insoluble. For this purpose 2 grms. of the sample may be put into a 100 cc. flask with about 80 cc. of 96 per cent. alcohol and heated on the water bath. After cooling, alcohol is added to the mark; the flask is well shaken and allowed to stand for the insoluble carbonate, &c., to subside. 50 cc. of the clear supernatant liquid are withdrawn and titrated with $\frac{N}{10}$ acid, as above, using phenolphthalein as indicator. Caustic soda may also be separated and estimated by extracting the sample (about 2 to 5 grms.) with 96 per cent. alcohol in a Soxhlet's apparatus (see *Analysis of Soap*, p. 759). This method is especially to be recommended when it is desired to determine very small quantities of caustic soda in soda ash.

Sodium Carbonate.—From the number of cc. of normal acid required to neutralise 1 gm. of total alkali, the number of cc. of the same acid required to neutralise the caustic soda in 1 gm. is deducted, and the difference calculated into sodium carbonate.

Example.—100 cc. of a solution (10 grms. per litre) of soda ash (= 1 grm.) neutralised 16 cc. of normal sulphuric acid.

1 grm. treated as above for caustic soda = 20 cc. $\frac{N}{10}$ = 2 cc. of normal acid.

$\therefore .040 \times 2 \times 100 = 8.00$ per cent. Na H O.

16 — 2 = cc. of normal acid corresponding to carbonate

$\therefore .053 \times 14 \times 100 = 74.20$ per cent. Na_2CO_3 .

Sodium sulphate is best determined (if necessary) gravimetrically. 2 to 5 grms. of the sample are dissolved in 100 to 200 cc. of water and the solution acidulated with hydrochloric acid. The liquid is boiled to expel carbon dioxide, precipitated with a slight excess of barium chloride and treated as described under *Standard Sulphuric Acid* (p. 735). 233 parts of barium sulphate correspond to 142 parts of anhydrous sodium sulphate.

Sodium chloride may be determined volumetrically by means of silver nitrate, using potassium chromate as an indicator. A decinormal solution of silver nitrate is prepared by dissolving 16.966 grms. of the pure salt in a litre of water. 1 cc. = 0.00355 grm. chlorine or 0.00585 grm. sodium chloride.

A given weight of the sample is dissolved in water and the solution exactly neutralised by $\frac{N}{10}$ nitric acid (having determined the total alkali the exact amount of nitric acid can be added direct), a few drops of a solution of potassium chromate are added and the $\frac{N}{10}$ silver solution run in from a burette until the liquid acquires a faint orange tint. If .585 grm. of the sample be taken for analysis, each cc. of $\frac{N}{10}$ silver nitrate corresponds to 1 per cent. of sodium chloride. The operation depends upon the fact that when silver nitrate is added to a neutral mixture of a chloride and chromate, silver chromate, which is of a crimson colour, is not formed until the whole of the chlorine present in the solution has combined to form silver chloride.

Sodium sulphide is indicated by the evolution of sulphuretted hydrogen when the sample is treated with an excess of hydrochloric acid. A more delicate test is sodium nitroprusside. Filter paper saturated with this reagent is dipped into a solution of the sample; if turned blue or violet, a sulphide is present. The amount may be determined by means of a standard solution of ammoniacal silver nitrate. This solution is prepared by dissolving 13.82 grms. of pure silver in dilute nitric acid, adding an excess of ammonia, and making up to a litre; 1 cc. = .005 sodium sulphide. The operation is performed by taking a weighed portion of the sample, dissolving in water, adding ammonia, and heating to boiling. The standard solution of silver is then run in until no further precipitate of silver sulphide takes place. The exact point can only be ascertained by filtering a few drops of the liquid, and testing the clear filtrate with a drop of the standard solution. For this and similar operations Beale's filter is very useful.

Sodium sulphite, together with sodium sulphide, may be determined by means of a decinormal solution of iodine (see p. 766). A weighed

amount of the sample is dissolved in water, and an excess of acetic acid added and a little starch solution. The iodine solution is then run in until a blue colour is produced. The amount of iodine required by the sulphide (already determined, if present) is calculated (1 cc. of $\frac{N}{10}$ iodine = .0039 grm. Na_2S), and deducted from the total amount consumed. The difference represents the sodium sulphite present. 1 cc. of $\frac{N}{10}$ iodine = .0063 grm. $\text{Na}_2\text{S O}_3$.

Except in very crude samples of soda-ash, the amount of sulphide and sulphite present is usually very small.

Oxide of Iron and Alumina.—In several applications of soda-ash, iron, if present, even in very small proportions, is a very objectionable impurity. If, for example, iron is present in soda-ash used for milling woollen cloth previous to dyeing, the fibre absorbs the oxide of the metal, which renders it impossible to obtain subsequently any bright shades with mordant colours. The oxide of iron present is also liable to work on to the cloth irregularly, and when such cloth is dyed, dark stains are produced.

The mixed oxides of iron and aluminium may be estimated by taking about 5 grms. of the sample, dissolving in water, and adding an excess of hydrochloric acid and a little nitric acid. The liquid is boiled and a *slight* excess of ammonia added. The precipitate is washed at first by decantation, collected on a filter, and thoroughly washed. It is then dried, ignited in a crucible, and weighed. The amount of *iron* may be determined by dissolving the mixed oxides in hydrochloric acid, or, preferably, by taking a fresh portion (about 5 grms.) of the sample, adding an excess of sulphuric acid, and boiling to expel carbon dioxide and any sulphuretted hydrogen or sulphur dioxide which may be present. The iron is then reduced to the ferrous state by means of pure zinc, as described under iron compounds (*Analysis of Mordants*, p. 775), and then titrated with $\frac{N}{50}$ potassium permanganate, each cc. of which corresponds to .00112 grm. Fe or .00160 grm. Fe_2O_3 . If the amount of iron present is very small, it is best determined by colour titration (see *Analysis of Water*, p. 752).

The amount of ferric oxide obtained is then deducted from the *mixed oxides*, the difference giving the *alumina* present, which, however, will probably include a little silica. The silica, if necessary, may be removed and estimated as described under *Analysis of Water*.

Lime may be estimated in the filtrate from the iron oxide and alumina by concentrating and adding a slight excess of ammonium oxalate. Since the amount of lime in any case will only be small, the calcium oxalate after thorough washing may be taken direct with the filter and ignited in a crucible. When the carbon of the filter has been completely burnt, the crucible is cooled, and a little pure sulphuric acid cautiously added. The excess of sulphuric acid is carefully driven off, and the calcium sulphate weighed: 136 parts of Ca S O_4 = 56 parts of Ca O .

Water.—Since the value of soda ash and other forms of sodium carbonate is determined by direct analysis, the estimation of water is not of much importance. In the case of a complete analysis, however, it should not be omitted. About 2 grms. of the sample are gently ignited to low redness in a crucible for 20 to 30 minutes. With a carbonated alkali the loss in weight may be directly calculated as water; but if caustic soda be present, it will, under ordinary conditions, absorb carbon dioxide with formation of carbonate. A dry soda ash containing caustic soda may be found to be heavier after ignition than before. If the operation is performed in a shallow platinum capsule, the caustic soda present will usually, in the course of an hour or so, become completely converted into carbonate. The conversion into carbonate may be ensured by addition of ammonium carbonate. The amount of CO_2 thus absorbed is calculated from the caustic soda present, and added to the loss in weight sustained on heating.

Analysis of Caustic Soda.—*Sodium Hydrate.*—The methods given under sodium carbonate are used also for caustic soda, the chief difference being that, whereas soda ash, &c., consist essentially of sodium carbonate with (possibly) small quantities of sodium hydrate, commercial caustic soda consists essentially of sodium hydrate with (possibly) small quantities of sodium carbonate.

Small quantities of carbonate in caustic soda may be conveniently estimated in the following manner:—A weighed amount of the sample is dissolved in about 200 cc. of cold water (free from CO_2), and a few drops of phenolphthalein added. Normal sulphuric acid is slowly and carefully added until the red colour is just discharged. At this point the caustic soda is completely neutralised, and the carbonate converted into bicarbonate. A few drops of methyl-orange are now added to the solution, and the addition of normal acid continued until an orange colour appears. The number of cc. of acid required *after* adding methyl-orange multiplied by 2 represents the amount of sodium carbonate present. Deducting that number from the total amount of acid consumed, the difference represents the sodium hydrate.

Example.—10 grms. of caustic soda were dissolved in 500 cc. of water. 50 cc. (= 1 gm.) were taken, diluted with cold (recently boiled) distilled water, and with phenolphthalein titrated with normal acid, as above described. 18 cc. were required. After adding methyl-orange, 8 cc. of acid was required.

1 cc. of normal acid = .040 gm. NaHO , or .053 gm. Na_2CO_3 .

$\therefore .053 \times 1.6 \times 100 = 8.48$ per cent. Na_2CO_3 .

$.040 \times 17.2 \times 100 = 68.80$ „ NaHO .

In place of the methyl-orange and phenolphthalein, Lunge* uses phenacetolin for estimating carbonates in presence of caustic alkalies. A solution of the indicator of suitable strength is prepared by dissolving 2 grms. in a litre of alcohol. This indicator is of a yellow

* *Journ. Soc. Chem. Ind.*, 1882, p. 56.

colour in presence of caustic soda and potash and free mineral acids, but red in presence of carbonates and bicarbonates. A few drops of the indicator are added to the solution to be tested, and normal acid added until the liquid acquires a rose-red tint. The volume of acid consumed corresponds to the amount of caustic alkali present. The addition of acid is now continued, the liquid becoming of a deeper red until suddenly it again becomes yellow. The second volume of acid added corresponds to the amount of sodium carbonate present.

Analysis of Potassium Carbonate.—*Pearl Ash*—*Potash*.

Analysis of Caustic Potash.—*Potassium Hydrate*.

The analysis of potassium carbonate and caustic potash does not differ essentially from that of the corresponding sodium compounds—

$$\begin{aligned} 1 \text{ cc. of normal acid} &= \cdot 069 \text{ grm. } K_2CO_3 \\ &= \cdot 056 \text{ „ } KHO \\ &= \cdot 047 \text{ „ } K_2O. \end{aligned}$$

Estimation of Potash by Platinum Chloride.—Since potash salts frequently contain considerable quantities of soda salts, either as natural impurities or adulterations, it is often necessary to estimate the amount of real potash present. The alkalimetric process, of course, would include soda, if present. The best method for estimating potassium in presence of sodium salts, although often considered too tedious and expensive for technical purposes, is undoubtedly by precipitation with platinum chloride. 5 grms. of the sample are dissolved in 500 cc. of water. If any insoluble matter be present it can be allowed to subside, and 25 cc. of the clear solution drawn off and introduced into a porcelain dish. A slight excess of hydrochloric acid is added, the dish being covered with a clock glass to prevent loss from effervescence. The clock glass is removed, taking care to wash the under side into the dish, an excess of platinum chloride added, and the solution evaporated *nearly* to dryness on a water-bath. The solution should remain highly-coloured yellow during the whole of the evaporation. If it becomes colourless, or nearly so, more platinum chloride solution must be added. The dish is allowed to cool (the residue should be still moist), and a mixture of alcohol and ether added in order to dissolve the excess of platinum chloride and sodium salts present. After 10 or 15 minutes the liquid is decanted through a small filter, and the operation repeated four or five times, until, in fact, the filtrate is not only colourless, but also leaves no more than the slightest stain when a drop or two are evaporated on a watch glass. The bulk of the precipitate will be left in the basin, but a small quantity will also be on the filter. The precipitate is transferred to a small weighed platinum or porcelain basin, and the small portion on the filter also washed in by means of hot water. The liquid is evaporated to dryness and dried at 100° C. in the water oven and weighed.

487 parts of the precipitate (K_2PtCl_6) correspond to 138 parts of K_2CO_3 .

If the substance to be analysed contains more than traces of sulphates, the sulphuric acid should be removed by barium chloride, otherwise the potassium platinum chloride is liable to be contaminated with sodium sulphate. This, however, may be prevented without practically affecting the accuracy of the results by having an excess of hydrochloric acid present, and allowing about half a cubic centimetre of liquid to remain in the dish before adding alcohol and ether. During the whole of the process, care should be taken to prevent access of vapours of ammonia, since ammonia also gives a double salt with platinum chloride, possessing similar properties to the potassium compound.

Estimation of Potash by Tartaric Acid.—2 grms. of the sample are washed into a small flask with about 25 cc. of water, and neutralised by tartaric acid. 50 cc. of a saturated solution of sodium bitartrate are added to the flask, and well shaken at intervals during the course of an hour. The precipitated potassium bitartrate is then collected on a small filter and washed with a cold saturated solution of potassium bitartrate. The filter and contents are put back into the flask, which may contain a little of the precipitate, hot water added, and the solution, with phenolphthalein as an indicator, titrated with normal caustic soda.

1 cc. of normal soda = .069 gm. K_2CO_3 or .056 gm. KHO .

Indirect estimation of Potash and Soda.—From .5 to 1 gm. of the sample is dissolved in water and a slight excess of hydrochloric acid. The solution is heated to the boiling point and, if any sulphates are present, barium chloride added. The barium sulphate is removed by filtration, and the excess of barium in solution precipitated by ammonium carbonate and ammonia. The filtrate from the barium carbonate precipitate is evaporated to dryness in a platinum dish, and the residue ignited to expel ammonium compounds. After cooling, the ignited residue is treated with hot water, and the solution filtered from any insoluble matter. The clear filtrate and washings, with addition of a little hydrochloric acid, are now evaporated to dryness in a weighed platinum dish, and the residue heated to about $180^\circ C$. in an air-bath, cooled, and weighed. This gives the mixed potassium and sodium chlorides present in the sample, and by estimating the combined chlorine, the amount of potassium and sodium chloride respectively can be calculated. The chlorides are dissolved in water and diluted to 500 cc.; 50 cc. are withdrawn and titrated with $\frac{N}{10}$ silver nitrate, as given under *Analysis of Sodium Carbonate* (p. 738). Each cc. = .00355 gm. Cl . The amount of potassium is found by multiplying the difference between the mixed chlorides and chlorine by 1.54, subtracting the chlorine and dividing by 0.63.

Analysis of Ammonia—Ammonium Hydrate.—Two qualities are known in commerce—viz., *gas liquor ammonia* and *sulphate ammonia*. The strongest *liquor ammonia* of commerce has a specific gravity of .880 and contains about 30 per cent. of N H_3 . A close approximation of the strength of a solution of ammonia may be ascertained by a careful determination of its density. For this purpose a specific gravity flask marked on the neck to hold 25 grms. of distilled water may be conveniently used. The dry flask is tared, carefully filled with the ammonia and again weighed. The weight of the sample thus obtained divided by 25 gives its specific gravity (water = 1), and on reference to tables the percentage of N H_3 is ascertained. The flask should be filled with distilled water and weighed to see that it really does hold exactly 25 grms. The specific gravity may also be taken by means of a delicate hydrometer.

The table on p. 209 shows the amount of N H_3 in solution of various densities according to Lunge and Wiernik.

Estimation of Ammonia by Titration.—The 25 cc. of ammonia used in taking the density, of which the weight is therefore known, may be diluted with water to 500 cc. Of this solution 50 cc. are withdrawn and, with methyl-orange as an indicator, titrated with normal sulphuric acid.

$$1 \text{ cc. of normal acid} = .017 \text{ gm. } \text{N H}_3$$

Example.—25 cc. of a sample of ammonia weighed 22.888 grms. Specific gravity, therefore, $= \frac{22.888}{25} = .9155$. The 25 cc. were diluted to 500 cc., and 50 cc. of this solution required 31.8 cc. of normal sulphuric acid.

$$\therefore \frac{.017 \times 31.8 \times 10 \times 100}{22.888} = 23.60 \text{ per cent. } \text{N H}_3.$$

Gas liquor ammonia may contain sulphides and tarry matter, which for some purposes are objectionable. Sulphides may be detected by the violet colour imparted to paper saturated with a solution of sodium nitroprusside. The presence of tarry matter is indicated by the smell which is gradually developed when a sample of ammonia is allowed to evaporate spontaneously. Commercial samples of ammonia, when neutralised by nitric acid, frequently develop a rose-red colour and a peculiar odour, due to the presence of minute quantities of certain organic bases.

Estimation of Combined Ammonia.—This may be done by distilling the sample with caustic soda, potash, lime, baryta, or magnesia, and collecting the ammonia in a known volume of standard acid and titrating back with standard alkali, or absorbing in an excess of hydrochloric acid, and estimating the ammonium chloride formed by platinum chloride.

1 gm. of the ammonium salt may be weighed out into a small flask of about 200 cc. capacity with 25 cc. of water. The flask is fitted with a cork having two openings, through one of which passes

a tapped funnel holding a strong solution (10 per cent.) of caustic soda. A glass-tube is inserted in the other opening, which should be inclined upwards at an angle of about 30° in order to prevent any fixed alkali being carried over mechanically with the ammonia. The tube is then bent downwards and passed through a cock into a flask of about 500 cc. capacity containing 40 cc. of normal sulphuric acid. The outlet of this receiving flask is fitted with a short wide tube containing glass-wool or glass beads, through which the standard acid has been poured. The distilling tube should be cut off at a sharp angle and reach nearly to the surface of the standard acid. Heat is applied to the small flask while the caustic soda solution is gradually run in. The liquid should be boiled for about 20 to 30 minutes. The small tube containing the glass-wool saturated with sulphuric acid is washed well with distilled water into the flask, and the residual acid determined by normal caustic soda, using methyl-orange as indicator.

Example.—1 gm. of ammonium sulphate was distilled, as above described, into 40 cc. of normal sulphuric acid. The acid remaining neutralised 25 cc. of normal soda; therefore, 15 cc. of acid were neutralised by the ammonia.

$$1 \text{ cc. of acid} = \cdot 017 \text{ gm. N H}_3.$$

$$\therefore \cdot 017 \times 15 \times 100 = 25\cdot 50 \text{ per cent. N H}_3.$$

If it is desired to estimate the ammonia gravimetrically, hydrochloric is used in place of sulphuric acid. After the distillation, the acid solution of ammonium chloride is poured into a porcelain dish, platinum chloride solution added, and the whole evaporated nearly to dryness on the water-bath. The double chloride of ammonium and platinum thus formed is treated in exactly the same manner as the corresponding potassium compound described under potash salts (p. 741). 445 parts of $(\text{N H}_4)_2 \text{Pt Cl}_6$ correspond to 34 parts of N H_3 .

Analysis of Sulphuric Acid.—*Oil of Vitriol.*—By a careful determination of its specific gravity, the strength of a sample of sulphuric acid may be approximately ascertained. The exact temperature at which the density is taken must be noted and, if necessary, corrections made, otherwise the results will be incorrect. A difference of 2°C. in the temperature may, if neglected, cause an error of 3 per cent. of sulphuric acid calculated from tables.

The tables given on pp. 148 and 149 show the strength of sulphuric acid of different densities.

Titration.—25 cc. of the sample accurately weighed are diluted with water to a litre. 25 cc. are withdrawn and titrated with normal caustic soda and methyl-orange. $1 \text{ cc.} = \cdot 049 \text{ gm. H}_2 \text{SO}_4$. The strength of the acid may also be ascertained by running the dilute solution from a burette into a solution of pure sodium carbonate. If 1·082 gm. of sodium carbonate is taken, the number of cc. of acid required to neutralise it contains exactly 1 gm. of $\text{H}_2 \text{SO}_4$.

Example.—25 cc. of sulphuric acid weighing 46 grms. were diluted to a litre.

1.082 Na_2CO_3 neutralised 22.5 cc. acid

22.5 cc. \therefore contain 1 grm. H_2SO_4

1,000 cc. \therefore „ 44.44 grms. H_2SO_4

$$\therefore \frac{44.44 \times 100}{46} = 96.60 \text{ per cent. } \text{H}_2\text{SO}_4.$$

Sulphuric acid of commerce is liable to contain numerous impurities, chief among which are sulphates of lead, iron, and soda, arsenious acid, and nitrogen acids. Arsenic is very often present in very considerable quantities in acid made from pyrites.

Sulphate of lead is indicated by the formation of a white precipitate on dilution with water. It may be estimated by taking about 25 cc. of the sample and adding 25 cc. of water and 50 cc. of alcohol. The liquid is filtered and the precipitate washed thoroughly with alcohol. The lead sulphate is dried, ignited in a porcelain crucible, and weighed. This determination, however, is not often necessary; it usually suffices to ignite about 10 grms. of the acid in a crucible and weigh the residue. The amount obtained, as a rule very small, of course includes sodium sulphate, if present.

Iron may be determined by igniting 10 to 20 grms. and treating the residue as given under *Analysis of Water* (p. 752).

The estimation of iron direct by reduction with zinc and subsequent titration with potassium permanganate cannot be recommended, since arsenic, if present, would seriously interfere with the reaction.

Nitrogen Acids.—Nitrogen compounds in sulphuric acid are especially mischievous in acid used for dissolving indigo, since a portion of the colouring matter is thereby destroyed, and the resulting extract is not so bright. They may be detected by carefully pouring a solution of ferrous sulphate into a test-tube containing the acid, the formation of a brownish-purple ring where the two liquids meet indicating the presence of oxides of nitrogen. A more delicate method, recommended by Thorp Whitaker,* is the following:—25 to 50 cc. of the acid are diluted with half the volume of water, and a drop of a 1 per cent. alcoholic solution of diphenylamine added. The liquid, on stirring with a glass rod, becomes coloured blue in the presence of nitrogen acids. The depth of the colouration is in proportion to the amount present. On standing, the colour gradually disappears.

Arsenic, if present in considerable quantities, is readily detected by diluting about 25 cc. with 150 cc. of water, and passing a current of sulphuretted hydrogen through the liquid. A yellow precipitate indicates arsenic, which may further be confirmed by treating the precipitate with a strong solution of ammonium carbonate, in which reagent arsenious sulphide is soluble.

If the yellow precipitate from a given weight of acid (about 50 grms.) be collected on a weighed filter paper, washed thoroughly,

* *Journ. Soc. Dyers and Col.*, 1885, p. 91.

dried at 100°C. , and weighed, the *amount* of arsenic present may be ascertained.

246 parts of the precipitate $\text{As}_2\text{S}_3 = 198$ parts of As_2O_3 .

Small quantities of arsenic are best detected and estimated by Marsh's test (p. 837).

Analysis of Sodium Sulphate.—Sodium sulphate is met with in the market as *salt-cake* and as *Glaubersalt*, or crystallised sodium sulphate. The latter (made by crystallising from salt-cake) is used in very large quantities in numerous dyeing operations. It is rarely necessary to make an examination of this substance unless it be to test for iron. Salt-cake usually contains about 95 per cent. of anhydrous sodium sulphate. The impurities are aluminium, calcium, and ferric sulphates, free sulphuric acid (as bisulphate), sodium chloride, insoluble matter, and water. The amount of sodium sulphate may either be estimated direct or ascertained by determining the amount of total impurities. These impurities may be estimated by the methods given under soda-ash (p. 737). For the direct estimation, Grossmann's process,* described in Sutton's *Volumetric Analysis*, is to be recommended. Briefly, about 4 grms. of the salt are dissolved in water, and an excess of barium hydrate added, which precipitates the sulphuric acid as well as oxide of iron and alumina. A stream of carbon dioxide is passed through an aliquot part of the filtered solution, and the liquid boiled, by which means the excess of baryta and any lime are removed. The liquid is again filtered, and an aliquot part titrated with standard sulphuric acid. 1 cc. of normal acid = $\cdot 071$ gm. Na_2SO_4 . Certain corrections are necessary, for details of which reference may be made to the works mentioned.

Analysis of Hydrochloric Acid (*Muriatic Acid*, *Spirits of Salt*).—The crude acid, obtained in enormous quantities as a secondary product in the manufacture of soda-ash, is usually of a yellow colour, due to the presence of organic matter and iron. Other impurities, which may be present are sulphuric acid, common salt, and arsenic. The strength of the pure acid may be conveniently ascertained by a determination of its density. The usual impurities, even in the crude acid, have little effect upon the density, although, of course, it is possible for the acid to be adulterated with common salt. The strongest solution of hydrochloric acid has a density of 1.21, and contains 43 per cent. HCl . The usual strength of commercial acid is 1.16 specific gravity, which contains 32 per cent. HCl . The table on p. 152 shows the percentage of HCl in solutions of various densities.

Titration of hydrochloric acid is performed in exactly the same manner as that of sulphuric acid. 50 cc. of the samples are weighed and diluted to a litre; 100 cc. of this solution titrated with normal caustic soda. 1 cc. = $\cdot 0365$ gm. HCl .

* *Chem. News*, vol. xli. (1880), p. 114.

Sulphuric acid is determined gravimetrically as in soda-ash.

Arsenic and iron may be determined as in sulphuric acid;

Sodium chloride by evaporation to dryness.

Analysis of Nitric Acid.—Two qualities of ordinary nitric acid are known in the trade—viz., *single aqua fortis*, having a density of 1.165, and containing 27 per cent. of HNO_3 ; and *double aqua fortis*, having a density of 1.325, and containing about 51 per cent. of HNO_3 .

The amount of HNO_3 in solutions of nitric acid of various densities is given in the table on p. 153.

Titration of Nitric Acid.—50 cc. of the sample are weighed and diluted to a litre, and 100 cc. of this solution taken for titration. 1 cc. of normal caustic soda = .063 grm. HNO_3 .

The usual impurities in commercial nitric acid are *sulphuric acid*, *hydrochloric acid*, and *sodium nitrate*. These may be readily detected and estimated by processes already described.

Analysis of Acetic Acid.—Acetic acid for technical purposes is obtained largely by the distillation of wood. The crude acid known as *pyroligneous acid* contains in addition to acetic a number of other acids as well as acetone, other ketones, wood oils, &c. By neutralising with lime and distilling the purified acetate of lime with a mineral acid, a purer acetic acid is obtained. Pure acetic acid has a density of 1.055, but a solution containing 43 per cent. of acetic acid also possesses the same density. On account of this anomaly a direct determination of the specific gravity cannot be utilised for ascertaining the strength of solutions of even pure acetic acid except in those cases where the density is lower than 1.055. By diluting the liquid with water, however, and taking the density again, one may ascertain whether the sample contains more or less than 77 per cent. of acid (see p. 155). With the crude acid, the specific gravity is no criterion whatever.

The table on p. 155 shows the percentage of acetic acid in solutions of various densities.

Titration of Acetic Acid.—In estimating acetic acid, *phenolphthalein* should be used as indicator. The end reaction is sharp, and even with highly-coloured liquids, if diluted, the termination is usually unmistakable. Litmus, methyl-orange, and other indicators are not suitable for acetic acid. 25 cc. of the sample are weighed and diluted to 500 cc.; 100 cc. are withdrawn and with addition of a few drops of phenolphthalein solution, titrated with normal caustic soda. 1 cc. = .060 $\text{C}_2\text{H}_4\text{O}_2$. In cases where the acid is of a very deep brown colour the following process recommended by Mohr may be used. About 5 grms. of the sample are treated with a known weight of pure calcium carbonate in excess. The liquid is boiled and filtered; the residue washed with hot water, and the undissolved calcium carbonate dissolved in a known excess of standard nitric acid and titrated back with caustic soda.

Example.—5.2 grms. were treated with 2 grms. of CaCO_3 , as above. To the residual CaCO_3 20 cc. of normal nitric acid were added, and it was found that 6 cc. of normal caustic soda were required to neutralise the liquid. Consequently, residual calcium carbonate neutralised 14 cc. of normal nitric acid = .7 gm. CaCO_3 . The acetic acid in 5.2 grms. of sample, therefore, neutralised 1.3 grms. of CaCO_3 = 1.56 grms. $\text{C}_2\text{H}_4\text{O}_2$ ($100 \text{ CaCO}_3 = 120 \text{ C}_2\text{H}_4\text{O}_2$).

$$\therefore \frac{1.56 \times 100}{5.2} = 30 \text{ per cent. of } \text{C}_2\text{H}_4\text{O}_2.$$

Commercial acetic acid is liable to contain as impurities and adulterations sulphuric acid and sulphates; hydrochloric acid and chlorides; iron, lead and calcium.

Sulphuric acid, free and combined, is detected and estimated by precipitation with barium chloride;

Hydrochloric acid, free and combined, by silver nitrate;

Calcium salts, by addition of ammonium oxalate;

Iron and Lead as in sulphuric acid.

Total solid matter may be determined by evaporating 20 cc. to dryness and drying in the air-bath at 110° .

Free mineral acids may be detected by moistening strips of white calico with the acid and drying at 90° to 100° . If hydrochloric or sulphuric acid be present the fibre is "tendered," disintegrated, or even charred. *Free sulphuric acid* may be detected and estimated by evaporating 10 to 50 cc. to a syrup, and, when cold, adding strong alcohol. Free sulphuric acid remains in solution, whereas sulphates are precipitated. The liquid is filtered and diluted with water, the alcohol boiled off and barium chloride added. The barium sulphate is then treated in exactly the same manner as previously described.

Estimation of Acetic Acid in Calcium Acetate and other Acetates.—Numerous processes have been proposed for estimating acetic acid in crude calcium acetate, but on account of a number of impurities many of these methods yield very inaccurate results. The best method is by distillation with phosphoric acid, as recommended by Stillwell & Gladding, and described in Allen's *Commercial Organic Analysis*, vol. i., p. 398. One gramme of the sample is washed into a flask or retort, having a capacity of about 100 cc., with 15 cc. of water. The neck of the retort is inclined slightly upwards to prevent anything being carried over mechanically. It is connected with a small Liebig's condenser, the inner tube of which, at its further extremity, passes downwards into a flask containing water (or standard caustic soda). The retort is fitted with a tapped funnel, through which is poured a solution of 5 grms. of glacial phosphoric acid in 10 cc. of water. Heat is now applied, and the liquid distilled until it is reduced to a volume of 5 or 10 cc., when 25 cc. of water are introduced through the funnel, and the distillation continued until the volume of liquid is again reduced to 5 or 10 cc. The addition of water and distillation are repeated three or four times, when the whole of the acetic acid will have passed over. The distillate is

titrated with $\frac{N}{10}$ caustic soda and phenolphthalein. Each cc. corresponds to .006 grm. of $C_2H_4O_2$. The phosphoric acid used must be free from nitric acid. If the sample or phosphoric acid contain chlorides, a little silver sulphate must be added to the contents of the retort to prevent hydrochloric acid distilling over.

Analysis of Oxalic Acid.—*Commercial oxalic acid* is not very often found adulterated, and impurities due to careless manufacture are not, as a rule, great. The amount of pure acid (in the absence of other acids and acid salts) may be accurately determined by standard alkali and phenolphthalein. 2 grms. is a convenient quantity to take for titration. Each cc. of normal caustic soda corresponds to .063 grm. of crystallised oxalic acid, $C_2H_2O_4, 2H_2O$.

Oxalic acid and oxalates may be determined in several ways by conversion in the first place into calcium oxalate. In the absence of other acids which are precipitated by calcium salts the liquid may be neutralised by ammonia and calcium chloride added. If phosphates, tartrates, sulphates, &c., are present the solution must be made slightly acid with acetic acid before adding the calcium chloride.

The calcium oxalate obtained may be converted into calcium carbonate by gentle ignition, and weighed as such; or it may be converted into calcium sulphate. It is better, however, to proceed according to one of the following methods:—

1. Wash the calcium oxalate well with hot water, transfer to a crucible, and ignite. The oxalate is converted into carbonate and, possibly, partly into oxide; but the results are the same in either case. The ignited residue is treated with an excess of normal nitric acid; the solution boiled and titrated back with normal caustic soda. Each cc. of normal acid consumed = .063 grm. $C_2H_2O_4, 2H_2O$.

2. Instead of drying and igniting the calcium oxalate, it may be transferred direct to a beaker, treated with water and dilute sulphuric acid and titrated with potassium permanganate, as described below.

Titration of Oxalic Acid and Oxalates by Permanganate.—In the absence of other oxidisable bodies, this forms a ready means of estimating oxalic acid, either free or combined. A decinormal solution of potassium permanganate containing 3.16 grms. of $KMnO_4$ per litre is prepared by taking rather more than that amount of the salt and standardising the solution with *pure* oxalic acid. For this purpose exactly .315 grm. of pure oxalic acid (or 50 cc. of $\frac{N}{10}$ solution) is taken and dissolved in about 50 cc. of water. About 50 cc. of dilute sulphuric acid are added, the liquid heated to 50° or $60^\circ C.$ and titrated with $\frac{N}{10}$ permanganate until a permanent pink coloration appears. If the permanganate is strictly decinormal 50 cc. will be required to produce this effect. If found too strong, it is diluted in the same manner as described under standard solution of sulphuric acid (p. 735).

The sample of oxalic acid or oxalate to be determined is then treated

in exactly the same way. Each cc. of $\frac{N}{10}$ permanganate corresponds to $\cdot 0063$ gm. of $C_2H_2O_4 \cdot 2H_2O$.

Impurities in Oxalic Acid.—Mineral salts are detected by igniting a portion of the sample; sulphates by dissolving in water and adding barium chloride and hydrochloric acid. Organic matter, other than oxalic acid, is present if the sample blackens on heating alone, or with concentrated sulphuric acid.

Analysis of Tartaric Acid and Tartrates.—The free acid is readily determined by normal caustic soda and phenolphthalein. About 2 grms. may be taken for analysis.

Each cc. of normal alkali = $\cdot 075$ gm. tartaric acid.

Impurities in tartaric acid may be detected as in oxalic acid.

Tartaric acid is sometimes, though not often, found adulterated with bisulphate of potash and alum.

Pure tartaric acid leaves no residue on ignition.

Acid potassium tartrate ($KHC_4H_4O_6$) occurs in various forms, as *cream of tartar*, *argol*, and *tartar*.

Warington, who, with Grosjean, has published many valuable papers on tartaric and citric acids, recommends the following methods for determining the value of commercial tartrates:—

1. (a) 5 grms. of the finely-powdered sample are heated with a little water and treated with about three-fourths of the total amount of normal caustic soda required to neutralise it. The liquid is boiled, and when nearly cold, neutralised exactly with a further quantity of normal soda, using phenolphthalein as indicator.

1 cc. of normal alkali = $\cdot 188$ gm. $KHC_4H_4O_6$.

(b) 2 grms. of the sample are ignited in a platinum crucible at a low red heat. The ash is transferred to a beaker or porcelain basin, and treated with a slight excess of normal sulphuric acid, and the liquid heated to boiling. The excess of acid is then determined by normal alkali. From the alkalinity of the ash of 1 gm. of tartar is subtracted the acidity of 1 gm. of unburnt tartar (both in terms of normal alkali), when the difference represents the neutralising power of the bases existing as *neutral tartrates*. 1 cc. of normal alkali is in this case equivalent to $\cdot 075$ gm. of tartaric acid as neutral tartrate, or $\cdot 113$ gm. of $K_2C_4H_4O_6$.

In presence of carbonates, this process does not give the separate amounts of acid and neutral tartrates, but the correct amount of total tartaric acid is obtained.

2. The following process depends upon the conversion of all the tartaric acid present into acid potassium tartrate.

From 2 to 4 grms. of the sample are moistened with a little water, and heated to boiling. The mixture is digested for about twenty minutes with an excess of neutral potassium oxalate, whereby any calcium tartrate is converted into oxalate, with formation of potassium tartrate. From 1 to 2 grms. of potassium oxalate should remain in excess. The liquid is now nearly neutralised with caustic potash, filtered through

a small filter, and the residue well washed. The filtrate and washings, containing the whole of the tartaric acid as normal potassium tartrate, are concentrated to about 60 cc.; 5 grms. of powdered potassium chloride are added, and the solution allowed to cool. A strong solution of 2 to 4 grms. of citric acid is then added, and the mixture stirred continuously for about ten minutes. The acid potassium tartrate which is thus precipitated is collected on a filter and washed (preferably by the aid of a filter pump) with a 5 per cent. solution of potassium chloride saturated with potassium bitartrate. The precipitate is transferred to the beaker in which the operation was conducted, dissolved in hot water, and titrated with normal alkali, using phenolphthalein as indicator.

Each cc. = .150 gm. tartaric acid.

Impurities.—In addition to natural impurities, ground tartar and argol are frequently found adulterated with various substances, such as *alum* and *bisulphate of potash*, and occasionally with *gypsum* and *chalk*.

Tartar substitute (*Tartar cake*, &c.) usually consists simply of a mixture of crude sodium sulphate and bisulphate. It is commonly prepared by heating a mixture of salt-cake and sulphuric acid. Some varieties consist of mixtures of sodium sulphates and real tartar.

Analysis of Citric Acid.—Citric acid in the free state is estimated by titration with normal soda and phenolphthalein (litmus is not suitable). 1 cc. of normal alkali = .07 gm. of crystallised citric acid, $C_6H_8O_7, H_2O$. Citric acid is liable to the same impurities and adulterations as tartaric acid (*q.v.*). Citric acid was formerly often found adulterated with tartaric acid, but, on account of the price, this practice is now practically obsolete.

Tartaric acid, however, may readily be detected by treating the sample with concentrated sulphuric acid, and heating the mixture in the water oven for about half an hour. Pure citric acid undergoes practically no change, whereas tartaric acid blackens. One per cent. of tartaric acid in citric acid may be thus detected. For determining the amount of tartaric acid in citric acid, Allen's* process is to be recommended. It depends upon the precipitation of acid potassium tartrate by a solution of potassium acetate in proof spirit.

Oxalic acid may be detected by neutralising with ammonia and adding acetic acid and calcium chloride, when, if present, a precipitate of calcium oxalate will be formed.

For further details regarding the analysis of acetic, oxalic, tartaric, and citric acids and their salts, Allen's *Commercial Organic Analysis*, vol. i., should be consulted.

ANALYSIS OF WATER.

It need scarcely be stated that the methods of analysis here given refer only to water for dyeing, scouring, and other technical purposes.

* *Chem. News*, vol. xxxi., p. 277.

The analysis of water for drinking purposes is quite a distinct subject.

A few qualitative methods of testing for the more commonly occurring substances in waters are given on p. 62.

Total Saline Matter.—About a litre of the water, accurately measured, is evaporated to dryness in a platinum dish, gently ignited and weighed. In many cases the weight obtained is a check upon the results of the analyses of the various constituents. In other cases, however, where such salts as calcium nitrate, magnesium carbonate, &c., are present in the water in considerable quantities, the weight of the total saline matter obtained direct is of little value.

Silica.—The residue is treated with dilute hydrochloric acid, taking care to cover the dish with a clock-glass to guard against loss from effervescence. The under side of the glass is rinsed with distilled water into the dish, and the solution evaporated to dryness. It is then heated in an air-bath to a temperature of about 130° for an hour to render the silica insoluble. When cold, strong hydrochloric acid is added in rather more than sufficient quantity to moisten the residue, and after standing 15 to 20 minutes, water is added and the liquid heated to boiling. It is then passed through a small iron-free Swedish filter, the residue of silica well washed, dried, ignited, and weighed. Grammes per litre multiplied by 70 equals grains per gallon.

Alumina and Oxide of Iron.—To the filtrate and washings from the silica, which need not measure more than about 100 cc., a slight excess of ammonia is added and the liquid kept near the boiling point until the smell of ammonia has disappeared. It is then filtered through a small Swedish paper, washed, dried, gently ignited, and weighed.

Oxide of Iron.—The ignited precipitate of oxide of iron and alumina is dissolved in a little concentrated hydrochloric acid and diluted with water to 100 cc. If the amount of iron is considerable (which is seldom the case), the iron may be reduced by metallic zinc and titrated by $\frac{N}{50}$ (.632 grm. per litre) permanganate (see p. 775). The amount of iron is usually so small that it is best estimated by means of colour-titration, with either potassium ferrocyanide or thiocyanate.

Estimation of Iron by Ferrocyanide.—A weak standard solution of iron is prepared so as to contain .00001 grm. of Fe per cc. For this purpose .7 grm. of ferrous ammonium sulphate (= .1 grm. Fe) is dissolved in a little water, acidulated with sulphuric acid, and oxidised either with nitric acid or potassium permanganate, and diluted to a litre. 100 cc. of this solution are then further diluted to a litre.

The operation may be conveniently performed in Nessler tubes. 10 to 50 cc. of the solution containing the ferric oxide (made up to 100 cc., as above described) are put into a Nessler tube; 1 cc. of strong hydrochloric acid (free from iron) and 1 cc. of a 2 per cent. solution of potassium ferrocyanide added, and filled to the 100 cc. mark with distilled water. A quantity of the weak iron solution

judged sufficient to produce the same depth of colour (1 to 5 cc.) is run into a similar tube, mixed with the same quantities of acid and ferrocyanide, and made up to 100 cc. After allowing a few minutes for the colour to develop, the cylinders are compared, and a fresh experiment made with more or less of the standard iron solution as may be required. Before adding the ferrocyanide, it is better to dilute the standard iron solution to the same extent as the liquid under examination. Nitric acid may be used in place of hydrochloric, but it is important to note that it should be free from nitrous acid. Nitric acid which has been exposed to light produces a green or greenish-yellow coloration with iron and ferrocyanide, instead of a blue. In place of Nessler tubes, the colorimeter may be used for this purpose.

Example.—The precipitate containing ferric oxide from a litre of water was dissolved in acid and diluted to 100 cc. 10 cc. of this solution produced the same depth of colour with potassium ferrocyanide as 6 cc. of the standard iron solution. One litre of the water, therefore, contains $0.0006 \times 10 = 0.0060$ gm. of Fe; = 0.42 grain of Fe = 0.6 grain of Fe_2O_3 per gallon.

Estimation of Iron by Thiocyanate.—This method is recommended by A. Thompson.* Exactly the same mode of working may be followed as with ferrocyanide. It is an exceedingly delicate reaction; 1 part of iron can be recognised in 50,000,000 parts of water.

Lime.—The filtrate and washings from the iron and alumina precipitate are made slightly ammoniacal, and the calcium precipitated as oxalate by ammonium oxalate. The liquid should be kept hot for some hours and filtered. The precipitate, after being washed, may be taken direct to a weighed crucible, heated at first very gently and then more strongly. When the carbon of the filter has completely disappeared the crucible is cooled and carefully treated with a drop or two of pure sulphuric acid, and again heated to drive off the excess. 136 parts of $\text{CaSO}_4 = 56$ parts of CaO .

Magnesia is determined in the filtrate and washings from the calcium oxalate precipitate. The liquid should be concentrated by evaporation to about 40 cc. A drop or two of a strong solution of citric acid is added, and when cold an excess of ammonia and about 5 to 10 cc. of a solution of sodium phosphate added. After standing 12 hours, the liquid is filtered, and the precipitate, consisting of ammonium-magnesium phosphate, well washed with a mixture of 1 part of strong ammonia and 6 parts of water in the cold. The filter and precipitate are dried and ignited separately in a crucible, at first gently, afterwards intensely, and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$. 111 parts of this precipitate = 40 parts of MgO .

Potash and Soda.—The alkalies are best determined in a fresh portion of the water. One litre is acidulated with hydrochloric acid, and concentrated to about 150 cc. The sulphuric acid, iron, alumina, and magnesia are removed by boiling with a little pure baryta water. The

* *Journ. Chem. Soc. (Tr.)*, 1885, p. 493.

excess of barium and the lime in the filtrate are removed by digesting with ammonium carbonate and oxalate. The filtrate is evaporated to dryness, and gently ignited; the residue treated with water, filtered from any insoluble matter, and the solution evaporated to dryness with hydrochloric acid. The residue of alkaline chlorides thus obtained is again gently ignited and weighed. If it be desired to determine the separate amounts of potash and soda present, the former may be estimated by platinum chloride, or the chlorine may be estimated in the mixed chlorides, and the potash and soda ascertained by calculation (see *Analysis of Potash Salts*, p. 742).

Sulphuric Acid as Sulphates.—A litre of water is acidulated with hydrochloric acid, evaporated to about 100 cc., and a slight excess of barium chloride added. The precipitate is collected on a small filter, dried, ignited, and weighed as BaSO_4 . 233 parts of $\text{BaSO}_4 = 80$ parts of SO_3 .

Chlorine is readily determined volumetrically by silver nitrate and potassium chromate. A convenient strength of silver nitrate is a solution containing 4.788 grms. per litre, each cc. of which = .001 gm. Cl. If $\frac{N}{10}$ silver nitrate is used, each cc. = .00355 gm. Cl. From 100 to 500 cc. of the water are measured into a porcelain basin, a drop or two of neutral potassium chromate added, and the liquid titrated with the standard silver nitrate solution, until the pure yellow colour changes to an orange yellow.

Carbonic Acid, Combined.—500 cc. are placed in a porcelain dish, and titrated with $\frac{N}{10}$ acid, using either methyl-orange or lackmoid, as indicator.

1 cc. of $\frac{N}{10}$ acid = .0022 gm. of CO_2 .

Carbonic Acid, Free, and as Bicarbonate.—This determination is of great importance for ascertaining the amount of lime or caustic soda required to be added in order to "soften" water. Pettenkofer's method is recommended for this purpose. 100 cc. of the water are put into a flask with 3 cc. of a strong solution of barium chloride, 2 cc. of ammonium chloride, and 45 cc. of a solution of barium hydrate of known strength. The flask is corked, the contents thoroughly shaken, and allowed to remain at rest for the precipitate of barium carbonate to subside. 50 cc. of the clear liquid are then withdrawn, and titrated with decinormal nitric acid. The number of cc. multiplied by 3, deducted from the number of cc. required to neutralise 45 cc. of barium hydrate direct, expresses the amount of CO_2 in the liquid in terms of decinormal acid. Each cc. of $\frac{N}{10}$ acid = .0022 gm. of CO_2 free, and as bicarbonate.

Example.—100 cc. of water were treated as above. (45 cc. of barium hydrate solution neutralised 35.1 cc. of $\frac{N}{10}$ HNO_3 .) 50 cc. of the clear solution (= one-third of whole) neutralised 9.2 cc. of $\frac{N}{10}$ nitric acid.

$35.1 - (9.2 \times 3) = 7.5$ cc. $\frac{N}{10}$ HNO_3 equivalent to free CO_2 in 100 cc. of water.

$\therefore .0022 \times 7.5 \times 10 \times 70 = 11.55$ grains of CO_2 per gallon.

Hardness.—The hardness of natural water is due almost entirely to the presence of salts of lime and magnesia (p. 64) which form insoluble stearates, palmitates, oleates, &c., with the fatty acids of soaps. For many years the hardness of a water has usually been determined by means of a standard solution of soap in weak alcohol, but chemists are now gradually adopting the *acidimetric* process. Both methods will be here described, but for general purposes decided preference is to be given to the acidimetric process. The soap test, devised by the late Dr. Clark of Aberdeen, gives in many cases (with waters containing principally sulphate of lime, for example) accurate and reliable results, but in numerous other cases, especially with waters highly charged with magnesium salts and free carbonic acid, the test is unsatisfactory. With any kind of water, if the hardness exceeds 16° (with magnesium waters 7°), the lathering does not proceed regularly, and in order to obtain concordant results, it is necessary to dilute with distilled water. Regarding this matter, A. H. Allen* writes:—

“This practice of diluting any hard water before titrating with soap solution raises the question: What is meant by the ‘hardness’ of water? Does it mean the soap-destroying power; or does it mean the proportion of calcium and magnesium compounds expressed in terms of calcium carbonate? If by the term ‘hardness’ the soap-destroying power of a water is to be understood, it seems very improper and unfair to dilute the water before making the determination. The laundress and manufacturer do not dilute the water they use, and hence to report a water as destroying as much soap as one containing, say, 30 grains of chalk per gallon, when, as a matter of fact, it does nothing of the kind, unless diluted before making the test, is misleading, and, in my opinion, is a practice which ought to be abandoned. On the other hand, if the ‘hardness’ is intended to represent the calcium and magnesium compounds in the water, the figures I have quoted suffice to show that the results are of the crudest possible character, quite unworthy of any one aspiring to the title of chemist.”

Although not to be recommended for general analytical purposes, the “soap-test” from its simplicity and rapidity is frequently of great service. When large quantities of water are being “softened” it is often necessary to make tests daily or more frequently. Again it is often required to make daily or hourly tests of the variations which take place in the hardness of the water from a well, stream, or other source. For these and similar purposes the soap-test is exceedingly useful.

Hardness by Soap-test.—Wanklyn’s method of working is perhaps the simplest, although for reasons mentioned above (and on p. 65), and in order that the results may be comparable with those obtained by the acidimetric method, the hardness of the water *per se* is not here taken into account. In other words, the degrees of hardness are intended to

* *Journ. Soc. Chem. Industry*, 1888, p. 797.

represent the number of grains of calcium and magnesium salts expressed in terms of calcium carbonate per gallon. According to Wanklyn's system the degrees of hardness are equal to grains of calcium carbonate per gallon, plus one.

The *soap solution* is conveniently prepared by dissolving 10 grms. of pure white Castile soap in 600 cc. of alcohol (90 per cent.) and diluting with water to a litre. This solution will probably be too strong and will require standardising. For this purpose a solution of *calcium chloride* is prepared by dissolving 1.11 grms. of the pure anhydrous salt in a litre of water. Or 1 grm. of pure calcium carbonate is carefully dissolved in a slight excess of hydrochloric acid, the solution evaporated to dryness, the residue treated with water and evaporated to dryness, and finally dissolved in water and diluted to a litre.

Standardising the Soap Solution.—10 cc. of the calcium chloride solution are introduced into a 10-oz. stoppered bottle and diluted with 60 cc. of distilled water. The soap solution is added in small quantities (about 1 cc.) at a time from a burette, and the bottle well shaken. When the lather begins to disappear somewhat slowly, smaller quantities are added at a time, and the bottle is placed on its side. The operation is complete when an unbroken lather remains permanent for five minutes. If the soap solution is of the correct strength 11 cc. will have been required to produce this effect. If less than 11 cc. the solution must be measured and carefully diluted with 50 per cent. alcohol until of the correct strength. The extra 1 cc. is required to give a permanent lather with 70 cc.* of pure water only. The *total hardness* of a water is ascertained by taking 70 cc. and titrating with the standard soap solution as above. The number of cc. minus one equals grains of CaCO_3 per gallon.

[The standard soap solution contains in each cc. just sufficient soap to precipitate 1 milligramme of CaCO_3 , and 1 milligramme bears the same relation to 70 cc. as 1 grain to a gallon.]

If more than 16 cc. (or more than 7 cc., if much magnesia is present) are required, a smaller quantity of water should be taken and made up to 70 cc. with distilled water.

Temporary and Permanent Hardness.—If a water undergoes no change in its soap-destroying power when boiled for some time, its hardness is said to be permanent, whereas, on the other hand, if the water becomes soft on boiling it is known as a temporary hard water. Both qualities are very frequently combined in the same water. The permanent hardness, due principally to sulphates of lime and magnesia, is determined by boiling 250 cc. or 500 cc. of water for half an hour, cooling quickly, and making up to the original volume with recently boiled and cooled water. 70 cc. of the filtered solution are then titrated with soap as above. It is evident that the difference be-

* This is not strictly correct under all conditions, but for practical purposes it is sufficiently near.

tween the direct titration and that after boiling, represents the precipitated carbonates of lime and magnesia previously held in solution by carbonic acid. This is known as the *temporary* hardness. It should not be overlooked that calcium carbonate itself is soluble in *pure* water to the extent of about 2 grains per gallon. Consequently according to the general acceptance of the terms "temporary" and "permanent" the hardness of a water containing 2 grains of calcium carbonate per gallon is permanent.

Hardness by the Acidimetric Process.—There are various modifications of applying this test. The *total* hardness may be obtained as follows:—100 cc. (or more) are treated with a slight excess of sodium carbonate and boiled down to about 25 cc. in a platinum or porcelain dish. The liquid is passed through a small filter and the residue washed with a little boiling (previously well boiled) distilled water, until the filtrate is neutral. The main portion of the precipitated calcium and magnesium salts remains in the dish, to which the washed filter is now added with about 50 cc. of distilled water. A drop or two of methyl-orange or lackmoid is added and a slight excess of $\frac{N}{10}$ nitric acid. After boiling a few minutes, the excess of acid is determined by $\frac{N}{10}$ alkali. Each cc. of $\frac{N}{10}$ acid consumed equals .005 grm. of CaCO_3 . The total amount of calcium and magnesium salts, expressed in terms of CaCO_3 , is thus obtained. In the case of very "soft" waters, 200 or 500 cc. should be taken, and $\frac{N}{50}$ acid and alkali might be substituted for decinormal.

Hehner,* evaporates a given volume of water to dryness, with a known amount of standard sodium carbonate in a platinum dish, extracts the residue with boiling distilled water, and determines the excess of sodium carbonate in the filtrate by weak standard acid. The sodium carbonate consumed represents the calcium and magnesium salts present in the water other than carbonates.

The hardness, due to *earthy carbonates* (in the absence of alkaline carbonates), may be readily ascertained by titrating 250 cc. or 500 cc. direct with $\frac{N}{10}$ acid in a porcelain dish.

In the case of an unknown water a given bulk should be boiled down exactly as described for the total hardness, omitting, however, the addition of sodium carbonate. The amount of standard nitric acid consumed by the precipitate thus obtained corresponds to calcium and magnesium carbonates.

On account of the slight solubility of earthy carbonates, already mentioned, in water *free* from carbonic acid, the carbonates obtained by the acidimetric method will not correspond exactly with the temporary hardness obtained by the soap test. The terms "temporary" and "permanent hardness" might, however, with advantage, be altogether dispensed with, and *hardness due to carbonates*, and *hardness due to salts other than carbonates* substituted. Permanent hardness

* *Analyst*, 1883, p. 77.

gives the impression that it cannot be removed, whereas, as a matter of fact, sulphates may be removed almost as easily as carbonates, although not by boiling.

Alkaline carbonates may be determined by titrating the filtrate (after boiling) with standard acid. 1 cc. of $\frac{N}{10}$ acid = .0053 grm. of Na_2CO_3 . The boiling must not take place in a glass vessel, otherwise an excess of alkali may be obtained.

ANALYSIS OF SOAP.

In many cases of soap analysis, it is merely necessary to estimate the amount of *water*, *fatty acids*, and *total alkali*. It is frequently of importance, however, to determine the amount of combined and uncombined alkali as well as uncombined fat.

A complete analysis would include the following determinations:—*Water*,¹ *uncombined fat*, *combined fatty acids* (calculated as anhydrides), *glycerin*, *resin*, *combined alkali*, *caustic alkali*, *sodium or potassium carbonate*, *chloride*, *sulphate* and *silicate*, *insoluble matter* (clay, sand, oxide of iron, &c.).

In addition to these determinations, it is often necessary to make an examination of the fatty acids in order to ascertain the kind of oils and fats which have been used in manufacturing the soap.

In taking portions for analysis, sections should be cut across the centre of a bar in the case of hard soaps, and the outer portions of a soft soap should be removed. The different weighings should be made at one time in order to guard against any irregularity caused by the sample losing water.

Water.—The usual method is to weigh from 3 to 5 grms. in the form of thin shavings on a clock glass or porcelain basin, and dry in an air-bath at a temperature of 110° until the weight is fairly constant. In the case of soft potash soap, a small glass rod should be weighed with the dish so that the soap may be stirred from time to time. Hard soaps require from 2 to 4 hours, but soft soaps frequently a much longer period.

Watson Smith* recommends the following modification:—From 5 to 10 grms. of soap in thin shavings are weighed into a counterpoised crucible containing a piece of glass rod flattened at the upper end and rough and jagged at the lower extremity. The crucible is placed on a sand bath which is gently heated by a Bunsen burner; the contents being continually stirred and turned over with the glass rod. The end of the operation is ascertained by removing the lamp and holding a piece of glass (a watch glass) over the crucible. When no more moisture becomes visible on the glass, the crucible is placed in a desiccator, cooled and weighed. Even if the soap burns a little, so penetrating is the odour of burnt soap that it will be immediately

* *Journ. Soc. Dyers and Col.*, 1884, p. 31.

detected, and the loss thus caused is usually quite inappreciable. The operation can be performed in about 20 minutes. With potash soaps and others containing glycerin, the results are not satisfactory, since it is difficult to ascertain exactly when the water is all given off.

Total Alkali.—5 grms. are dissolved in about 200 cc. of hot water, and, with either methyl-orange or cochineal as indicator, titrated with $\frac{N}{5}$ sulphuric acid, each cc. of which corresponds to .0062 gm. Na_2O or .0094 gm. K_2O . The fatty acids set at liberty have no action upon either of these indicators.

If the amount of *potash* be required when both potash and soda are present, a given weight of soap is decomposed with hydrochloric acid and the filtered solution treated with platinum chloride as on p. 741.

Uncombined Alkali.—This may exist in a soap either as *caustic* or *carbonate*, or both. The best method of analysis consists in extracting the dry soap with strong alcohol. About 3 grms. in fine shavings are weighed and dried in a water oven for about 2 hours. A water oven is preferable to an ordinary air-bath, since any caustic alkali which may be present is less liable to be converted into carbonate during the process of drying. In order to avoid this source of error altogether it is necessary to use a specially constructed bath arranged to prevent access of carbon dioxide. After drying, the soap is placed in a plaited filter and introduced into a Soxhlet's tube, the lower end of which is connected to a small wide-mouthed flask containing pure alcohol, to which has been added a few drops of phenolphthalein and sufficient caustic potash (a drop or two of $\frac{N}{10}$ KHO will usually suffice) to render the liquid faintly pink. The upper extremity of the Soxhlet's tube is connected with an inverted Liebig's condenser and the small flask immersed to the neck in water, which is kept at or near the boiling point. The alcohol boils and the vapour condenses in the Soxhlet's tube. A portion of the soap and caustic alkali (if present) dissolves, and the solution flows over by means of the small syphon into the flask. The operation must be continued until the whole of the soap has dissolved. The time required varies considerably, according to the nature of the soap and the rate at which the alcohol distils. From two to four hours will be required on an average. The alcoholic solution contains the pure soap and any glycerin and caustic alkali which may be present. The solution will be pink if caustic alkali is present. It is titrated with $\frac{N}{10}$ acid until the colour disappears. Each cc. = .004 gm. NaHO or .0056 gm. KHO . The residue insoluble in alcohol may contain, in addition to sodium or potassium carbonate, chlorides, sulphates, silicates, and insoluble matter. It is dissolved in water and titrated with $\frac{N}{10}$ sulphuric acid and methyl-orange. Each cc. = .0053 gm. Na_2CO_3 or .0069 gm. K_2CO_3 . For a more complete analysis of the residue see Dr. Leed's scheme (p. 764).

Uncombined alkali is sometimes determined by precipitating a solu-

tion of soap with a strong solution of pure sodium chloride and titrating the filtrate with standard acid. The results are not accurate as pointed out by C. R. A. Wright and C. Thomson,* but, excepting soaps made from cocoa-nut and palm oil, fairly approximate figures are quickly obtained.

Combined Alkali.—The alkali existing as carbonate (also silicate, if present) and caustic is subtracted from the total alkali, when the difference gives the amount of alkali combined with fatty acids as soap. The combined alkali may also be determined in the alcoholic solution after neutralising any free caustic alkali or free fatty acid in the presence of phenolphthalein. Water is added to the solution which with a few drops of methyl-orange is titrated with standard acid. The acid thus consumed corresponds to combined alkali. The combined alkali may further be calculated from the amount of standard alcoholic potash required to neutralise the liberated fatty acids in the method described below. The total alkali having been determined, this method affords a means of estimating the uncombined alkali by difference.

Fatty Acids.—In a careful determination of all the other constituents of a soap, the fatty acids, as recommended by Watson Smith,† may conveniently and with accuracy be ascertained by difference.

A method commonly used in practice, consists in decomposing a solution of 5 grms. of soap with sulphuric or hydrochloric acid. If the liberated fatty acids are soft, a weighed amount of hard white wax or paraffin is added, and when cold the cake is carefully removed, dried, and weighed. It is often difficult to remove the whole of the fatty acids completely from the beaker, and in some cases a considerable portion of the fatty acids is soluble in water. This difficulty may be partially overcome by adding salt to the liquid. Or the amount of fatty acid in the liquid may be approximately ascertained by dividing the solution into two parts; titrating one portion with caustic soda and methyl-orange and the other with caustic soda and phenolphthalein. The difference between the two titrations will give the amount of fatty acids present in terms of standard soda.

A preferable plan to the above for estimating fatty acids is the following:—About 3 grms. of the soap are dissolved in 50 to 60 cc. of water and introduced into a stoppered separator of a capacity of 200 cc. The soap is decomposed with a slight excess of hydrochloric acid, and when cold about 50 cc. of ether added and the whole well shaken. When the two liquids have separated, the acid solution is run off and the ether solution washed two or three times in the separator with cold distilled water. The solution of fatty acids is then carefully poured into a small weighed wide-mouthed flask, and the separator well rinsed out with pure ether. The ether is distilled off and the residue of fatty acids dried in a water oven and weighed. In order to get rid of water (usually present in the residue) a little strong alcohol is added

* *Journ. Soc. Chem. Ind.*, 1885, p. 625. † *Journ. Soc. Dyers and Col.*, 1884, p. 31.

before the flask is put into the oven. By either process, the weight obtained will of course include any uncombined fat or unsaponifiable matter, if present. This must be either estimated separately and deducted, or the dried soap must be previously treated with petroleum ether. The operation, however, is not often necessary in practice.

The fatty matter, weighed as free fatty acids, exists in the soap in combination with potash or soda. In a complete analysis it is, therefore, necessary to calculate the fatty acids into their corresponding anhydrides. In the majority of cases multiplying by .97 answers the purpose.

In the *Journal of the Society of Dyers and Colourists*, 1885, p. 58, Rawson describes a volumetric process for determining fatty acids in soap. The fatty acids from a weighed amount of soap are dissolved in about 50 cc. of hot neutral alcohol, and, with phenolphthalein as an indicator, titrated with a standard solution of alcoholic potash. Knowing the saponification equivalent of the fatty acids (readily ascertained as described below), the percentage may be easily calculated. The operation may be readily performed by decomposing the soap with hydrochloric acid, and shaking up with ether in a separator, as already described, but instead of evaporating off the ether and weighing the residue of fatty acids, the ethereal solution is mixed with about 50 cc. of neutral alcohol, and titrated direct with $\frac{N}{5}$ alcoholic potash and phenolphthalein.

Example.—3 grms. of soap were decomposed by hydrochloric acid, and the liberated fatty acids neutralised 35 cc. of $\frac{N}{5}$ alcoholic potash. The saponification equivalent of the fatty acids was found to be 276; therefore 1 cc. of $\frac{N}{5}$ K H O = .0552 grm. of fatty acids.

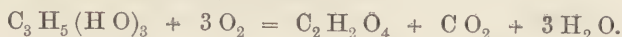
$$\therefore \frac{.0552 \times 35 \times 100}{3} = 64.40 \text{ per cent. of fatty acids.}$$

Free Fat and Unsaponifiable Oil.—This may be performed by extracting the dried soap in a Soxhlet's tube with light petroleum ether, which has been previously distilled on a water bath, but an objection to this plan is that soap is not quite insoluble in the volatile solvent, and a preferable method, as recommended by Allen, consists in dissolving the soap in water and shaking the solution with ether in a separator. When the liquids have separated (which frequently takes a considerable time), the aqueous solution of soap is run off, and the ether solution washed with water and poured into a tared flask. The ether is distilled and the residue dried and weighed. The aqueous solution of soap should be shaken up a second time with ether, unless the amount of unsaponified matter present is very small.

Glycerin.—In Leed's scheme (p. 764) glycerin is determined gravimetrically, but at 100° C. glycerin volatilises somewhat freely, and the results are consequently too low. In the absence of sugar, it may be conveniently estimated by Benedikt & Zsigmondy's process,* origi-

* *Journ. Soc. Dyers and Col.*, 1885, p. 245.

nally suggested by Wanklyn, and also investigated by Fox. The method is based upon the fact that when glycerin is oxidised in alkaline solution with potassium permanganate, it is converted into oxalic acid, carbon dioxide, and water:—



In the case of soap, 10 grms. are dissolved in water, and decomposed with dilute hydrochloric acid. The solution freed from fatty acids is diluted to 400 cc., and made strongly alkaline with 10 to 15 grms. of caustic potash. A strong solution of potassium permanganate is added until the colour of the liquid changes from green to bluish-black. The mixture is boiled for about an hour, when the excess of potassium permanganate is destroyed by the addition of a strong solution of sodium sulphite, and the liquid filtered. The filtrate is acidulated with acetic acid and boiled, and the oxalic acid present precipitated by calcium acetate. The precipitate of calcium oxalate thus obtained may contain silica and calcium sulphate, and cannot, therefore, be weighed as carbonate. The precipitate may be ignited, and the lime estimated by titration with standard nitric acid and caustic soda, as on p. 749; or, preferably, the calcium oxalate is dissolved direct in dilute sulphuric acid, and the oxalic acid estimated by titration with $\frac{\text{N}}{10}$ permanganate, as on p. 749. 56 parts of CaO, or 126 parts of $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ correspond to 92 parts of glycerin.

Resin.—Gladding's method (see Leed's scheme, p. 764) has generally been considered the best for estimating resin in soaps, although the process is open to several objections. It is necessary to make a considerable allowance for the solubility of silver *oleate*, and Wright and Thompson* have shown that for different fats this is by no means constant. Gladding makes an allowance of .00235 gm. for every 10 cc. of ether solution evaporated.

E. Twitchell, in the *Journal of Analytical Chemistry* (1891, p. 379), has recently described a process which has been found to give very satisfactory results. 2 to 3 grms. of fatty and resin acids (obtained by decomposing soap with dilute HCl) are dissolved in ten times their volume of absolute alcohol in a flask, and dry HCl gas passed through in a moderate stream. The flask is set in a vessel containing water to keep it cool. The hydrochloric acid is rapidly absorbed, and after about forty minutes the ethers of the fatty acids separate and float on the surface. The flask is removed and allowed to stand half an hour longer, to ensure a complete combination of the alcohol and fatty acids. The liquid is diluted with five volumes of water, and boiled until the acid solution is clear, the ethers, with resin acids in solution, floating on the top. On cooling, some light petroleum-naphtha is added, and the whole transferred to a separator. The acid solution is run off, and the naphtha solution (about 50 cc. in volume) washed with water. A

* *Chem. News*, vol. liii. (1886), p. 165.

solution of .5 grm. of caustic potash, 5 cc. of alcohol, and 50 cc. of water is poured into the separator, and the whole agitated. The resin acids are thus saponified, and the ethers of the fatty acids remain in the naphtha. The solution of resin soap is run off and decomposed with hydrochloric acid, the resin collected, dried, and weighed. Instead of weighing the resin, it may be determined volumetrically by means of standard alkali. In this case, ether is used in place of naphtha, and the washing with water must be continued until the wash water is no longer acid. 50 cc. of neutral alcohol are then added to the ethereal solution of resin and ethers in the separator, and with phenolphthalein as indicator, titrated with standard potash or soda. The ethers of the fatty acids, under these conditions, are not affected by the alkali. The combining weight, or saponification equivalent, of the resin acids is taken at 346.

The scheme on next page for the complete analysis of soap (by A. R. Leeds) is taken from the *Chemical News*, vol. xlviii. (1883), p. 166.

Examination of Fatty Matter in Soap.—In the analysis of soap it is frequently desired to ascertain what kind of oils and fats have been used in its manufacture. This is much the most difficult part of the examination. Much information may generally be obtained from a determination of the saponification equivalent of the fatty acids; their specific gravity, and their melting and solidifying points. A few brief descriptions only will be here given. For fuller particulars, reference should be made to such works as Allen's *Commercial Organic Analysis*, vol. ii.

Saponification Equivalent.—About 5 grms. of the fatty acids (free from water) are dissolved in 60 to 70 cc. of hot *neutral* alcohol, and, with phenolphthalein as indicator, titrated with $\frac{N}{2}$ alcoholic potash. The weight in milligrammes of the fatty acids taken, divided by half the number of cc. of $\frac{N}{2}$ K H O required, gives the saponification equivalent.

Specific Gravity is best determined at 100° C. in a small Sprengel's tube of a capacity of about 7 cc. The weight of the dry tube and that of water contained in it at 15°·5 are first ascertained. The tube is then filled with the melted fatty acid and placed in the mouth of a conical flask containing water, which is kept briskly boiling. The oil expands, and the excess flows out in drops from the capillary orifice. When the expansion ceases, any oil adhering to the orifice is carefully removed by filter paper, the tube removed, dried, cooled, and weighed. The weight thus obtained divided by the weight of water at 15°·5 will give the density or specific gravity of the fatty acids at 100° compared with water at 15½° as unity.

Melting Point of the fatty acids may be conveniently observed in the following manner:—A piece of quill-tubing is drawn out into a long capillary tube, which is cut into lengths of about 3 inches. One of these is dipped into the molten fatty acid, and a *small* quantity,

Extract is uncombined fat. Dry at 100° and weigh.		Weigh out 5 grammes. Dry at 110°. Loss corresponds to water.	
Treat with petroleum ether.		Treat with alcohol.	
Residue is soap and mineral constituents. Treat with alcohol.		Residue. — Na_2CO_3 , NaCl , Na_2SO_4 , sodium silicate, starch, and insoluble residue. Wash with 60 cc. water.	
H_2SO_4 used corresponds to free alkali. Calculate as NaHO .	Add a large excess of water and boil off the alcohol. Decompose with excess of normal H_2SO_4 . Boil, filter, and wash.	Filtrate. — Na_2CO_3 , NaCl , Na_2SO_4 , and sodium silicate. Divide into four equal parts.	
	Residue. — Fatty acids and resin. Dry at 110° and weigh. Dissolve an aliquot part in 20 cc. strong alcohol, and, using phenolphthalein as an indicator, saponify with soda in slight excess. Boil, cool, and add ether to 100 cc. Decompose with AgNO_3 by adding in fine powder, and shake well for ten minutes. Allow to settle.	Residue. — Starch and insoluble residue. Dry the filter and weigh. The weight is the starch and insoluble residue.	
	Filtrate. — Combined soda and glycerin. Titrate with normal soda solution.	Starch. — Convert the starch into $\text{C}_6\text{H}_{12}\text{O}_6$. Titrate with Fehling's solution. Subtract the weight of starch found, and the difference is the insoluble mineral constituents.	
H_2SO_4 used corresponds to combined soda in soap. Calculate as Na_2O .		Normal H_2SO_4 , and calculate as Na_2CO_3 .	
After titration evaporate to correspond on the water-bath. Treat with absolute alcohol. Evaporate the alcoholic solution to dryness in a tared dish and weigh as glycerin.		Sodium silicate. Decompose with HCl and determine soda combined in silicate and silica.	
Precipitate is stearate, palmitate, and oleate of silver.		Sodium silicate. Decompose with HCl and determine soda combined in silicate and silica.	
Solution. — Resinate of silver. Filter 50 cc. from the total 100 cc. Decompose with 20 cc. HCl (1:20). Allow the AgCl to settle, and evaporate an aliquot part of the ethereal solution in a tared dish. Dry at 110° and weigh. After applying correction for oleic acid, the weight corresponds to the resin. This weight subtracted from the combined weight of fatty acid and resin gives the fatty acids.		Sodium silicate. Decompose with HCl and determine soda combined in silicate and silica.	

occupying a space of about a tenth part of an inch, drawn up and allowed to solidify. After about an hour (not less) the tube is attached to the stem of a thermometer by means of a small india-rubber ring (a small bit cut off a piece of india-rubber tubing answers well) in such a manner that the fatty acid is close to the bulb. The thermometer with the tube is immersed in a small beaker of water, which is itself immersed in a conical flask filled with water. A Bunsen flame is placed under the flask, and the thermometer and substance in the small tube carefully watched. The temperature should not be allowed to rise more than about $\frac{1}{2}^{\circ}\text{C.}$ per minute. When the fatty acid melts (which is usually quite sharp) the temperature is at once observed and recorded.

Solidifying Point of fatty acids is best determined as described by Allen in the following manner:—A test tube, about 5 inches in length and $\frac{3}{8}$ inch in diameter, is fitted with a ring or collar of cork, by which it is fixed in the mouth of an empty flask. The melted fatty acid is poured into the (warmed) tube till it is about two-thirds filled, and a delicate thermometer, previously warmed, is suspended freely in the liquid, so that the bulb may be wholly immersed. When the fatty acids begin to solidify at the bottom of the tube the thermometer must be attentively observed. The operator then stirs the contents of the tube slowly, by giving the thermometer a circular movement, first three times to the right, and then thrice to the left. The first effect of the agitation is to cause the thermometer to fall slightly, but subsequently a sensible rise takes place, and the mercury remains stationary for at least two minutes. The temperature thus indicated is the solidifying point of the substance, and the results obtained are remarkably constant. The following table, chiefly compiled from figures in Allen's *Commercial Organic Analysis*, will be found useful in drawing conclusions from data obtained by the above methods:—

SOURCE OF FATTY ACIDS.	Saponification equivalent or com- bining weight.	Specific gravity at 100°C. compared with water at 15.5° .	Melting point. $^{\circ}\text{C.}$	Solidifying point. $^{\circ}\text{C.}$
Olive oil,	279	.842	26	21
Cotton-seed oil, . . .	277	.848	36	30-35
Rape oil,	320	.842	19.5	15-18
Linseed oil,	307	.858	18	13-17
Tallow,	273	.836	45	43-50
Palm oil,	270	.837	47-50	42-46
Cocoa-nut oil,835	24	20.5

The *scouring value* of soap is sometimes determined by means of a standard solution of calcium chloride. This solution (1.11 grm. Ca Cl_2 per litre) is prepared as described on p. 756 for determining the hardness of water. 5 grms. of soap are dissolved in 300 cc. of 90 per cent. alcohol, and diluted to 500 cc. with water. The operation

is performed exactly in the same manner as in estimating the hardness of water. 10 cc. of the calcium chloride solution are mixed with 60 cc. of distilled water and titrated with the soap solution, until a permanent lather is obtained.

When two or more samples of soap are treated in this manner, the relative scouring value of the samples is inversely proportional to the number of cc. consumed. The results are only approximately correct.

ANALYSIS OF BLEACHING COMPOUNDS.

Analysis of Chloride of Lime.—This compound, known also as *bleaching powder*, is used in immense quantities in the bleaching of cotton, linen, and other vegetable fibres. It may be considered to consist practically of a mixture of calcium hypochlorite, calcium chloride, and calcium hydrate, although in the dry state its composition is considered by Odling and Lunge to be represented by the formula $\text{Ca}(\text{OCl})\text{Cl}$ —that is, calcium chloro-hypochlorite. Bleaching powder usually contains small quantities of calcium chlorate, and, in some cases, where sufficient care has not been taken in the manufacture, this compound may exist to the extent of from 8 to 10 per cent. The value of chloride of lime for bleaching purposes depends entirely upon the amount of available chlorine present. Chlorate of calcium is of no value as a bleaching agent.

Penot's method of analysis is based upon the conversion of an alkaline arsenite into an arsenate, for which purpose a decinormal solution of arsenite is prepared.

Preparation of Decinormal Sodium Arsenite Solution.—4.95 grms. of pure resublimed arsenious oxide and 25 grms. of pure sodium carbonate are dissolved in about 250 cc. of water. The arsenious oxide must be in fine powder, and the liquid heated to boiling to promote solution. When quite clear it is cooled and diluted to one litre. The strength of the solution may be verified by titration with a carefully prepared *decinormal solution of iodine*. For this purpose 12.7 grms. of pure resublimed iodine are dissolved in the cold in a solution of 18 grms. of pure potassium iodide, and diluted to a litre. 10 cc. of the arsenious solution are placed in a porcelain basin, and a few drops of starch solution added. The iodine solution is then run in from a burette with constant stirring until a permanent blue colour appears. In this and similar operations with iodine solution, it is not absolutely necessary to use starch as an indicator. The faintest excess (certainly less than $\frac{1}{10}$ cc.) of iodine, without starch, may be known by the liquid acquiring a pale yellow colour. If 10 cc. are required, the solution is strictly decinormal.

Titration of Bleaching-Powder Solution.—10 grms. of the sample of bleaching powder are weighed out into a mortar, and rubbed into a thin cream with water. After allowing the coarser particles to sub-

side, the turbid liquid is poured into a litre flask, and the particles in the mortar again ground up with more water. This is repeated three or four times, when the whole of the 10 grms. will have been transferred to the litre flask. Water is then added to the mark, and the flask well shaken. 50 cc. of the turbid liquid, immediately after shaking, are withdrawn by means of a pipette and titrated with $\frac{N}{10}$ arsenite solution until a drop of the liquid ceases to give a blue or violet colour with prepared iodised starch paper. This paper may be readily prepared by saturating filter paper with a solution made by boiling about $\frac{1}{4}$ gm. of starch, $\frac{1}{4}$ gm. of potassium iodide, and $\frac{1}{10}$ gm. of sodium carbonate with 50 cc. of water.

1 cc. of $\frac{N}{10}$ sodium arsenite = .00355 gm. Cl.

Example.—10 grms. bleaching powder made up to a litre, as above described. 50 cc. (= .5 gm. sample) required 42.2 cc. of $\frac{N}{10}$ As_2O_3 .

$$\therefore \frac{.00355 \times 42.2 \times 100}{.5} = 29.96 \text{ per cent. of chlorine.}$$

Bunsen's method depends upon the oxidation of sodium thiosulphate. It records the amount of chlorine present as chlorate as well as hypochlorite; consequently, it is not so well adapted for the valuation of bleaching powder as Penot's method. If both methods are performed, the difference between the two results shows the amount of chlorine present as chlorate.

A decinormal solution of *sodium thiosulphate* is prepared by dissolving 24.8 grms. of the pure crystallised salt, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, in a litre of water. This may be standardised either by the decinormal solution of iodine already described, or, preferably, by a decinormal solution of potassium bichromate, containing 4.917 grms. of $\text{K}_2\text{Cr}_2\text{O}_7$ in a litre. For this purpose 25 cc. of $\frac{N}{10}$ $\text{K}_2\text{Cr}_2\text{O}_7$ are run into a porcelain basin; 10 cc. of a 10 per cent. solution of potassium iodide, an excess of dilute hydrochloric acid, and about 200 cc. of water are added. The thiosulphate solution is then gradually added from a burette until the solution is nearly colourless, when a little starch solution is added, and the titration continued until the blue colour disappears. If strictly decinormal, 25 cc. of thiosulphate will be required, each cc. of which corresponds to .00355 gm. Cl. In this reaction the bichromate liberates an equivalent amount of iodine from the excess of potassium iodide used.

Titration of Bleaching Powder.—20 cc. of the solution prepared as above described (10 grms. per litre) are diluted with about 200 cc. of water, and treated with 10 cc. of potassium iodide solution and a slight excess of hydrochloric acid. The liquid is then titrated with $\frac{N}{10}$ thiosulphate exactly in the same manner as in standardising with bichromate.

Lunge* has devised a gasometric method depending upon the

* *Journ. Soc. Chem. Ind.*, 1890, p. 22.

evolution of oxygen when a solution of bleaching powder or hypochlorite is mixed with peroxide of hydrogen.

Bleaching liquors and other hypochlorites may be analysed in exactly the same manner as chloride of lime.

Analysis of Sodium Bisulphite.—The principal bleaching agent for wool and silk is sulphurous acid, applied for the most part in the form of gas (sulphur dioxide) obtained by burning sulphur in "stoves" (see pp. 136, 140, 144). Solutions of bisulphite of soda and other bisulphites are, however, often used in certain cases. A large quantity of sodium bisulphite is also used in the preparation of the so-called "hydrosulphite" or hyposulphite indigo vat.

Sulphur Dioxide, SO_2 .—Undoubtedly the best method of estimating the total amount of sulphur dioxide in sulphurous acid, sulphites, and bisulphites is by means of iodine, as described by Giles and Shearer in the *Journal of the Society of Chemical Industry*, 1884, p. 197. The older methods of analysis by means of iodine were liable to serious errors.

About 0.5 grm. of the sample (in the case of liquid sodium bisulphite it is better to take 10 cc. and dilute to 500 cc. with distilled water, which has recently been boiled and cooled), is weighed out and introduced at once into a known excess of decinormal iodine solution, and, after stirring, the excess of iodine is determined by a decinormal solution of sodium thiosulphate, as described under chloride of lime (p. 767).

The number of cc. of $\frac{N}{10}$ thiosulphate are deducted from the number of cc. of $\frac{N}{10}$ iodine taken and the remainder calculated to sulphur dioxide—

$$1 \text{ cc. of } \frac{N}{10} \text{ iodine} = .0032 \text{ grm. of } \text{SO}_2.$$

Example.—10 cc. liquid bisulphite of soda, sp. gr. 1.25, were diluted with recently boiled and cooled water to 500 cc. 20 cc. of this solution (= .4 cc. or .5 grm. of sample) were introduced into a beaker containing 35 cc. of $\frac{N}{10}$ iodine. It was then found that 5.5 cc. of $\frac{N}{10}$ thiosulphate were required.

$$\therefore \frac{.0032 \times 29.5 \times 100}{.5} = 18.88 \text{ per cent. of } \text{SO}_2.$$

An excellent gravimetric process for estimating sulphur dioxide in sulphites is described by Giles and Shearer in the paper above mentioned.

Indicators used in acidimetry are very differently affected by sulphurous acid and sulphites. With *phenolphthalein*, for example, normal sodium sulphite, Na_2SO_3 , reacts neutral, whereas the acid sulphite (bisulphite), NaHSO_3 , is neutral to *litmus*, *cochineal*, and *methyl-orange*. With litmus and cochineal the reaction is uncertain, but with methyl-orange it is sharp and distinct. *Normal sulphites* may, therefore, be readily determined by titrating with normal sulphuric acid and methyl-orange.

Free sulphurous acid and sulphurous acid existing as bisulphite, may,

on the other hand, be determined by using standard caustic soda and phenolphthalein. If commercial bisulphite of soda be diluted with water and a few drops of a solution of methyl-orange added, the liquid will be red if *free* sulphurous acid is present, and the amount of standard alkali required to produce the neutral point, will be a measure of the sulphurous acid above that required to form bisulphite. If, on the other hand, the liquid is decidedly yellow, *normal* sulphite is present, the *amount* of which may be determined by standard acid.

Analysis of Hydrogen Peroxide.—Peroxide of hydrogen in solution is sold containing ten or twelve volumes of oxygen. This denotes that one volume of the liquid contains peroxide in such quantity as to evolve ten or twelve volumes of oxygen respectively when reduced to water. The value of a sample depends upon the amount of available oxygen present.

Estimation by Iodine and Thiosulphate.—Kingzett* has shown that the best method of estimating peroxide of hydrogen is by means of iodine and thiosulphate. The peroxide in an acid solution liberates an equivalent of iodine from potassium iodide, which is thus estimated by $\frac{N}{10}$ thiosulphate. About 10 cc. of the sample are mixed with 30 cc. of a mixture of equal volumes of water and sulphuric acid, and an excess of potassium iodide added. After standing about five minutes, the liberated iodine is titrated with $\frac{N}{10}$ thiosulphate and starch, as described under chloride of lime (p. 767).

1 cc. of $\frac{N}{10}$ thiosulphate = .0017 grm. of $H_2 O_2$ or .0008 grm. of O_2
 1 grm. oxygen = 697.5 cc. at 0° C.

Estimation by Potassium Permanganate.—In the absence of other bodies acted upon by permanganate, this forms a ready means of determining the value of hydrogen peroxide. A measured quantity of the sample is acidulated with sulphuric acid and $\frac{N}{10}$ permanganate added until a faint pink colour appears.

1 cc. of $\frac{N}{10}$ permanganate = .0017 grm. of $H_2 O_2$.

Gasometric Determination.—Coulamine† recommends the following process as a rapid means of estimating hydrogen peroxide:—10 to 20 cc. are neutralised with ammonia and diluted to 250 cc. 25 cc. of this solution are introduced into a gas absorption tube graduated for 50 cc. in $\frac{1}{10}$ cc., a few crystals of potassium permanganate wrapped in tissue paper are added, the tube quickly closed by the thumb and vigorously shaken. When the reaction is complete, the tube is inverted over water and the volume of gas evolved read off.

This method, however, is not very exact.

* *Journ. Chem. Soc. (Tr.)*, 1880, p. 792.

† *Journ. Soc. Dyers and Col.*, 1886, p. 7.

ANALYSIS OF MORDANTS, FIXING AGENTS, &c.

ALUMINIUM COMPOUNDS.

Analysis of Alum.—The two principal varieties of aluminium alums are potash alum, $\text{Al}_2\text{K}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$, and ammonia alum, $\text{Al}_2(\text{NH}_4)_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$.

Potash alum contains 10.76 per cent. of alumina, Al_2O_3 , and ammonia alum contains 11.27 per cent. Potash alum is rather more soluble than ammonia alum; 100 parts of water at 20°C . dissolve 15.1 parts of the former and 13.6 parts of the latter. In other respects, so far as the dyer is concerned, they may be considered as identical.

Ammonia alum is readily distinguished from potash alum by evolving ammonia when boiled with caustic soda.

Impurities.—Alum in the crystallised state cannot well be adulterated, but iron and free sulphuric acid may be present as impurities.

Iron may be readily detected by adding a mixture of potassium ferro- and ferricyanides, which quickly produce a blue colour with iron. A greyish-blue colour is *gradually* developed with *pure* alum. Tannic acid may also be used as a test for iron.

Free Sulphuric Acid.—For the detection of free acid in alums and aluminium sulphate, Watson Smith* recommends the use of ferric acetate, the red colour of which is destroyed by a trace of free acid. The operation is best performed in a porcelain dish. Congo-red, a colouring matter which turns blue with free acids, has been frequently recommended for the same purpose, but it is not a very delicate test.

A preferable method (and one which admits of a ready quantitative determination) is to treat the powdered sample with strong alcohol containing a little phenolphthalein and rendered pink with addition of potash. If free sulphuric acid be present the colour is removed, and by titrating the filtered solution with $\frac{N}{10}$ alkali the amount present is readily ascertained.

Alum purchased in the ground state may contain a variety of substances—such as common salt, sodium sulphate, and excess of water. The best method of ascertaining the value of such samples is to determine the amount of alumina by precipitation with ammonia. 1 grm. is weighed out and dissolved in about 200 cc. of water, a considerable amount of ammonium chloride is added and a *slight* excess of ammonium hydrate. The liquid is kept near the boiling point for some time until the smell of ammonia disappears, when it is filtered and the precipitate well washed with boiling water. The precipitate is dried and ignited in a crucible and weighed as Al_2O_3 .

Analysis of Aluminium Sulphate (*Cake Alum, Concentrated Alum, Patent Alum*).—It contains in a pure state 15 per cent.

* *Journ. Soc. Dyers and Col.*, 1884, p. 35.

of alumina, and may be examined in exactly the same manner as alum.

For detecting and estimating free sulphuric acid in aluminium sulphate Beilstein and Grosset* recommend the following process:—1 to 2 grms. are dissolved in 5 cc. of water and 5 cc. of a cold saturated solution of ammonium sulphate added. After a quarter of an hour 50 cc. of 95 per cent. alcohol are added, and the whole filtered and washed with 50 cc. of the same liquid. The alcoholic liquid may then be examined for free acid as in alum.

Aluminium sulphate crystallises with difficulty, and is more liable to contain impurities than alum. In many cases it is considered by dyers not to give such good results as common alum; this may probably be due to irregular composition and to the absence of sulphate of potash or ammonia.

Aluminium sulphate is largely used in the manufacture of other aluminium mordants.

Analysis of Aluminium Acetate (*Red Liquor, Red Mordant, Pyrolignite of Alumina*).—It is usually sold at a strength of about 24° Tw., and may be prepared by the action of aluminium sulphate upon lead or calcium acetate. The best method of examining samples of red liquor is by means of comparative dye-tests. For this purpose equal weights of cotton are impregnated with equal quantities of the samples to be examined in the same manner as described under *Application of Aluminium Mordants* (p. 234), and subsequently dyed with alizarin or some other mordant-colour. The dyed material is then dried, and the swatches compared.

Estimation of Alumina.—About 5 grms. of the sample are evaporated to dryness in a platinum dish, and the residue gently ignited to destroy organic matter. When cold, the residue is dissolved in hydrochloric acid, and the alumina precipitated by ammonia, as described under *Alum*.

Estimation of Acetic Acid.—This is best performed by distillation with phosphoric acid, and titration of the distillate with normal caustic soda and phenolphthalein, as described under *Calcium Acetate* (p. 748).

CHROMIUM COMPOUNDS.

Analysis of Bichromates.—The most important chromium mordants are undoubtedly potassium and sodium bichromates.

Potassium bichromate, $K_2Cr_2O_7$, known to the trade also as "*bichrome*," or "*chrome*," in the crystallised state is usually nearly pure, although recently several samples have been found to contain a considerable amount of potassium sulphate. This was probably due to imperfect manufacture, since the potassium sulphate so found had evidently been present in the liquor during crystallisation.

* *Journ. Soc. Chem. Ind.*, 1890, p. 416.

100 parts of water at 15° C. dissolve 10 parts of potassium bichromate. It crystallises without water, and contains 68.09 per cent. of CrO_3 . Sodium bichromate, which has only appeared on the market in recent years, has in a great many instances displaced the more expensive potassium salt. There are two chief varieties of commercial sodium bichromate—viz., the crystalline and the amorphous or lump. Crystallised sodium bichromate, $\text{Na}_2\text{Cr}_2\text{O}_7, 2\text{H}_2\text{O}$, contains nearly the same amount of chromic acid as potassium bichromate—viz., 67.70 per cent. The dry lump also usually contains about the same amount (some more, others less); but in place of water of crystallisation it contains sodium sulphate and other impurities. The crude varieties of sodium bichromate often contain considerable quantities of normal chromate, which is a much less effective mordant than the acid salt.

Sodium bichromate is a very deliquescent salt, and is very soluble in water. 100 parts of water at 15° C. dissolve about 110 parts of the anhydrous salt.

Estimation of Chromic Acid.—The usual method of estimating chromic acid in chromates and bichromates consists in adding an excess of ferrous ammonium sulphate to an acidulated solution of the sample and titrating the residual ferrous salt with decinormal potassium bichromate. In lieu of this mode of procedure the following plan can be recommended:—Weigh out 5 grms. of the sample and dissolve in a litre of water, with which solution fill a burette. In the case of sodium bichromate, in order to obtain a fair average sample, it is preferable to weigh out 25 grms. and dissolve in 500 cc., and then, after shaking, take out 100 cc. and dilute to a litre. 1 gm. of pure granulated ferrous ammonium sulphate is then weighed out and dissolved in a little water in a porcelain basin and 50 cc. of a 10 per cent. solution of sulphuric acid added. The solution of bichromate is then added during constant stirring with a glass rod until a drop of the liquid ceases to give a blue or greenish-blue coloration when brought in contact with a drop of potassium ferricyanide solution on a porcelain slab. 1 gm. of ferrous ammonium sulphate reduces .0854 gm. of CrO_3 ; consequently, the number of cc. of the solution required contains this amount of chromic acid.

Example.—5 grms. of potassium bichromate were dissolved in a litre of water. Of this solution, 1 gm. of ferrous ammonium sulphate required 25.2 cc.

$$\begin{aligned} \therefore 25.2 \text{ cc.} &= .0854 \text{ gm. of } \text{CrO}_3 \\ \therefore 1000 \text{ cc.} &= 3.388 \text{ grms. of } \text{CrO}_3 \\ \frac{3.388 \times 100}{5} &= 67.76 \text{ per cent. of } \text{CrO}_3. \end{aligned}$$

Chromic acid may be determined *gravimetrically* by conversion either into chromic oxide or chromate of lead. The former process is carried out by dissolving .5 gm. of the sample of bichromate (or by taking 100 cc. of the solution above mentioned) in a little water, adding

hydrochloric acid, and heating either with alcohol or sulphurous acid. The excess of alcohol or sulphurous acid is boiled off and the green solution diluted to about 200 cc. treated with a *slight* excess of ammonia. The precipitate is collected on a filter, well washed, dried, ignited, and weighed as Cr_2O_3 . 153 parts of Cr_2O_3 correspond to 201 parts of CrO_3 .

Estimation of Normal Chromate.—Potassium bichromate rarely contains normal chromate, but, as previously stated, the sodium compound frequently contains considerable quantities. At the present time, however, it is not so prevalent as it was a few years ago. Three methods for estimating normal chromate will be described, but, when present in small quantities, preference is given to the first process.

1. M'Culloch's process* depends upon the fact that free chromic acid, when shaken up with peroxide of hydrogen and ether, imparts a blue coloration to the ether; whereas neither chromate nor bichromate produce any effect. If bichromate alone is taken, a drop or two of acid is sufficient to produce the blue colour, whereas, if normal chromate is present, acid must be added in sufficient quantity to convert it into bichromate. The following plan of carrying out the operation is recommended:—2·5 to 5 grms. of the sample are dissolved in 40 to 50 cc. of water, and the solution introduced into a stoppered cylinder, holding about 120 cc. 10 cc. of hydrogen peroxide (10 vols.) and about 20 cc. of ether are added and the contents shaken. (If free chromic acid be present the ethereal layer will be of a blue colour.) A decinormal solution of sulphuric acid is now added in small quantities at a time with frequent agitation until the ether is tinged faintly blue, which is best seen against a white background. Each cc. of $\frac{N}{10}$ acid corresponds to ·01005 grm. of CrO_3 as normal chromate = ·01625 grm. of Na_2CrO_4 or ·01945 grm. of K_2CrO_4 .

If the hydrogen peroxide contains acid, this must be taken into account.

2. In the paper above mentioned, M'Culloch refers to the direct determination of bichromate by means of standard soda and phenolphthalein, and thence by deducting chromic acid so found from the total chromic acid, calculating the amount of normal chromate present. He correctly points out that the end reaction is not sharp and precise, but if an excess of caustic soda be added and the liquid titrated back with standard acid this difficulty is altogether overcome.

1 cc. of $\frac{N}{10}$ soda = ·01005 grm. of CrO_3 as bichromate.

3. R. T. Thomson† has shown that bichromate of potash or soda is neutral to lackmoid, whilst normal chromate is alkaline. Normal chromate may, therefore, be estimated in bichromates by standard acid and lackmoid paper. Free chromic acid may be likewise determined by using decinormal soda.

* *Chem. News*, vol. lv. (1887), p. 2.

† *Ibid.*, vol. lii. (1885), p. 29.

Examples.—A sample of impure bichromate of soda gave 70·60 per cent. of total chromic acid, Cr O_3 .

By Method 1.—2·5 grms. with hydrogen peroxide and ether required 30·6 cc. of $\frac{N}{10}$ sulphuric acid.

$$\therefore \frac{0.01005 \times 30.6 \times 100}{2.5} = 12.30 \text{ per cent. of } \text{Cr O}_3 \text{ as chromate,}$$

\therefore by difference = 58·30 per cent. of Cr O_3 as bichromate.

By Method 2.—50 cc. of a 1 per cent. solution (=·5 grm.) were treated with a few drops of phenolphthalein and 35 cc. of $\frac{N}{10}$ caustic soda. 6·1 cc. of $\frac{N}{10}$ acid were then required to produce a pure yellow solution.

$$\therefore \frac{0.01005 \times 28.9 \times 100}{.5} = 58.03 \text{ per cent. of } \text{Cr O}_3 \text{ as bichromate,}$$

and by difference = 12·52 per cent. of Cr O_3 as chromate.

By Method 3.—100 cc. of a 1 per cent. solution (= 1 grm.) were titrated with $\frac{N}{10}$ sulphuric acid, using lackmoid paper as an indicator. 12·6 cc. were required.

$$\therefore 0.01005 \times 12.6 \times 100 = 12.66 \text{ per cent. of } \text{Cr O}_3 \text{ as chromate,}$$

and by difference = 57·94 per cent. of Cr O_3 as bichromate.

Sulphuric acid as potassium or sodium sulphate in bichromates may be directly determined by precipitation with barium chloride in a dilute and acid solution, but more accurate results are obtained by previously reducing the chromic acid to chromic oxide by means of alcohol and hydrochloric acid.

Chrome Alum possesses a similar constitution to common alum—viz., $\text{K}_2 \text{Cr}_2 (\text{S O}_4)_4, 2\frac{1}{2} \text{H}_2 \text{O}$. It is liable to contain tarry organic matter, calcium sulphate, and sodium sulphate as impurities. The chromium oxide may be determined by precipitation with ammonia as alumina in common alum.

Chromium Acetate is usually sold in solution at 30° to 36° Tw. containing about 15 to 17 per cent. of chromium acetate. It may be examined in precisely the same manner as aluminium acetate (p. 771).

IRON COMPOUNDS.

Analysis of Ferrous Sulphate.—This salt, known also as *copperas* and *green vitriol*, crystallises with seven molecules of water. It was formerly largely used in conjunction with logwood for dyeing blacks upon wool, but has been almost entirely replaced by bichromates. It is now used principally in cotton dyeing. Exposed to moist air, ferrous sulphate becomes covered with a brown film of basic ferric sulphate. For some purposes this is considered rather advantageous than otherwise, but if used for *vat indigo dyeing* the ferric sulphate is merely so much waste material.

Ferrous iron is readily estimated, either by a standard solution of bichromate or of permanganate. The estimation by bichromate is merely the reverse of the method already described for *Chromic Acid* (p. 772). The estimation by permanganate is exceedingly simple, and is carried out as follows:—

Preparation of Decinormal Permanganate Solution.—3.156 grms. of pure dry potassium permanganate are dissolved in a litre of distilled water. The solution requires standardising, since perfectly pure potassium permanganate is not easily obtainable. This is most readily performed by means of pure granulated ferrous ammonium sulphate. 0.7 gm. of this salt (= 0.1 gm. of iron) is dissolved in about 100 cc. of water in a porcelain basin, and 50 cc. of a 10 per cent. solution of sulphuric acid added. The permanganate solution is now gradually run in from a burette, with constant stirring, until the liquid becomes of a faint pink colour. If strictly decinormal, 17.85 cc. will be required.

Instead of taking ferrous ammonium sulphate, the permanganate may also be standardised by means of pure clean iron wire. 0.1 gm. is introduced into a small flask fitted with a bent glass tube and Bunsen's valve (see below, *Estimation of Total Iron*), and dissolved in dilute sulphuric acid. When dissolved, the liquid is allowed to cool, and titrated with the permanganate solution, as above described.

Ferrous ammonium sulphate, a salt frequently mentioned in this division, has a composition represented by the formula $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and contains exactly one-seventh of its weight of iron. It is prepared by mixing equivalent proportions of pure ferrous sulphate and ammonium sulphate (dissolved separately), and allowing the double salt to crystallise out. It occurs in commerce in crystals and in a fine granulated form. For use in chemical analysis, the latter is to be preferred. It should be preserved in a well-stoppered bottle. If there is any doubt about its purity, a weighed amount should be dissolved in water, with addition of a little sulphuric acid; the solution oxidised by nitric acid, and the iron estimated gravimetrically (see *Analysis of Ferric Sulphate*). Another portion should be dissolved in a little water, and tested for ferric iron by means of potassium thiocyanate.

Estimation of Ferrous Oxide.—1 gm. of the sample of ferrous sulphate (or 100 cc. of a 1 per cent. solution) is dissolved in about 100 cc. of water and 50 cc. of a 10 per cent. solution of sulphuric acid added. The solution is then titrated in a porcelain dish with $\frac{N}{10}$ potassium permanganate until a faint pink colour remains for about half a minute after stirring. 1 cc. of $\frac{N}{10}$ permanganate = .0072 gm. of FeO or .0278 gm. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

Estimation of Total Iron.—1 gm. is washed into a small flask with about 50 cc. of water; 5 to 10 cc. of strong sulphuric acid and a rod of zinc free from iron are then introduced. The flask is fitted with a cork and bent glass tube, to which is attached a Bunsen's valve. This merely consists of a short piece of india-rubber tubing closed at one end with a glass rod and having a longitudinal slit in the centre. Steam and hydrogen can by this arrangement easily escape from the flask, but air is unable to enter. The flask is inclined at an angle of about 45° and

gently heated. When the reduction is complete (known by a drop of the liquid producing no coloration with a drop of potassium thiocyanate) recently boiled and cooled water is allowed to enter the flask, and the liquid titrated with $\frac{N}{10}$ permanganate as above. If the rod of zinc has not thoroughly dissolved, it must be carefully removed and washed before titrating with permanganate. The difference between this titration and the direct titration represents the amount of iron present in the ferric state. 1 cc. of $\frac{N}{10}$ permanganate = .008 gm. of Fe_2O_3 .

Alumina may be detected in ferrous sulphate by boiling with addition of sulphuric and nitric acids to oxidise the iron, and adding an excess of *pure* caustic soda. The liquid is boiled and filtered, and to the filtrate hydrochloric acid and ammonia added, when, if alumina be present, a white gelatinous precipitate will be obtained.

Acetate of iron is sold in solution under the names of *iron liquor*, *black liquor*, and *pyrolignite of iron*.

The best practical method of ascertaining the value of acetate of iron is to make careful dye-trials, as with ferric sulphate. The total amount of *iron* and *acetic acid* present may be determined in the same manner as alumina and acetic acid in aluminium acetate (p. 771). The iron may also be determined by igniting to destroy organic matter; dissolving the residue in hydrochloric acid, reducing with zinc and titrating the solution with permanganate.

Impurities.—Commercial acetate of iron may contain ferrous sulphate, ferrous chloride, sodium sulphate, and sodium chloride. Sodium salts may be detected and estimated by adding an excess of ammonia and evaporating the filtrate to dryness, and igniting. The amount of ferrous sulphate or ferrous chloride, in the absence of alkaline salts, may be determined by estimating the sulphuric or hydrochloric acid present.

Analysis of Ferric Sulphate.—Solutions of ferric sulphate, more or less basic, with and without ferrous sulphate, are largely used in cotton and silk dyeing under the name of *Nitrate of iron*.

The solutions usually have a strength of about 80° Tw., and contain about 10 per cent. of iron.

If ferrous sulphate is present a blue precipitate will be obtained with potassium ferricyanide.

Estimation of Total Iron.—25 cc. (measured in a specific gravity bottle, and weighed) are diluted to 500 cc. 25 cc. are withdrawn and diluted to about 200 cc. If any iron is present in the ferrous state, it is preferable to add a few drops of nitric acid, and boil for some minutes. A slight excess of ammonia is added, and the liquid filtered. The precipitate should be washed two or three times with hot water by decantation before bringing it wholly on to the filter. The precipitate may be either dried, ignited, and weighed as Fe_2O_3 or, dissolved in sulphuric acid, reduced by zinc, and titrated with $\frac{N}{10}$ permanganate, as given under ferrous sulphate.

In the absence of nitric acid or nitrates, the 25 cc. of the diluted solution may be reduced direct, and titrated with permanganate.

1 cc. of $\frac{N}{10}$ permanganate = .0056 grm. of Fe.

Estimation of Ferrous Iron.—5 to 10 cc. of the sample are weighed, diluted with water, and acidulated with sulphuric acid. The solution is then titrated with $\frac{N}{10}$ permanganate.

1 cc. = .0056 grm. of Fe, or .0072 grm. of Fe O.

The amount of ferric oxide is obtained by deducting ferrous iron from the total and calculating into Fe₂O₃.

Sulphuric acid is best determined by acidulating the filtrate from the ferric oxide precipitate with hydrochloric acid, and adding barium chloride. If barium chloride is added direct to the ferric sulphate solution the barium sulphate is liable to be contaminated with iron.

Hydrochloric acid should also be determined, after removal of the oxide of iron by ammonia, by acidulating the solution with nitric acid and adding silver nitrate.

Sodium salts may be detected and estimated by adding ammonia, and evaporating the filtrate to dryness, and igniting the residue. If iron compounds only were present nothing more than a trace would remain after ignition.

Relation of Acid to Base.—In the analysis of ferric sulphate one of the most important matters is to determine the relative proportion of total acid and ferric oxides present. For most purposes, commercial "nitrate of iron" or ferric sulphate should contain less acid than that necessary to form normal ferric sulphate. Some samples contain a slight excess of acid. The amount of acid in combination with iron (as well as any free acid, if present) is best determined by taking 2 to 5 grms. of the sample, diluting with about 200 cc. of water, and adding a slight excess of normal solution of sodium carbonate. The liquid is boiled and filtered, and the precipitate well washed with hot water. The excess of sodium carbonate is then estimated by normal sulphuric acid and methyl-orange. Each cc. of normal sodium carbonate = .040 grm. of S O₃.

Example.—2.5 cc. = 3.56 grms. of ferric sulphate were treated with 22 cc. of normal Na₂CO₃. The filtrate required 4 cc. of normal H₂SO₄.

∴ $\frac{.040 \times 18 \times 100}{3.56} = 20.22$ per cent. of S O₃, combined with ferric and ferrous oxides.

The amount of S O₃ required to combine with the found percentages of ferric and ferrous oxides to form normal sulphates is calculated and compared with the actual amount of acid present. Instead of using sodium carbonate, boiling and filtering as above given, fairly good results may be obtained by titrating direct with normal caustic soda and phenolphthalein, as in the case of tin mordants (p. 779); but the end reaction is not very distinct.

The following figures show the results of analyses of a few samples of average ferric sulphate or "nitrate of iron" :—

	1.	2.	3.	4.
Specific gravity,	1.410	1.402	1.405	1.345
Equal to degrees Twaddle, . .	82°	80°	81°	69°
Total iron,	11.80	10.88	10.97	9.59
Ferric oxide,	16.86	15.45	12.00	12.72
Ferrous oxide,	none	.15	3.32	.86
Sulphuric acid (S O ₃),	16.61	17.20	16.75	16.20
Hydrochloric acid (H Cl), . . .	1.64	.06
Total acid combined with iron } in terms of S O ₃ , }	20.05	17.30	16.96	16.40
Calculated S O ₃ required to } form normal sulphates, . . . }	25.30	23.39	22.74	20.31

"Nitrate of iron" should always be tested practically by experimental dye-trials. If intended for cotton dyeing the following plan might be adopted. Swatches of calico or cotton yarn, each weighing 10 grms., are thoroughly wetted out and worked together for about an hour in a decoction of sumach or myrabolans. The swatches are taken out, the excess of liquid removed by shaking, and each piece put into a dilute solution (5 cc. to 250 cc.) of the sample of "nitrate of iron" to be examined. After 20 to 30 minutes the pieces are taken out, well washed, dried, and compared.

TIN COMPOUNDS.

Analysis of Stannous Chloride.—This salt crystallises with 2 molecules of water, Sn Cl₂, 2 H₂ O. It is commonly known in the dye-house as *tin crystals*.

Stannous chloride is occasionally found adulterated with zinc or magnesium sulphates or zinc chloride.

Sulphates may be readily detected by addition of hydrochloric acid and barium chloride.

Zinc and magnesia may be detected in the filtrate after precipitating the tin as sulphide by a current of sulphuretted hydrogen in an acid solution.

Estimation of Tin.—About .25 grm. of the sample is dissolved in a little water containing hydrochloric acid, and mixed with 50 cc. of a 10 per cent. solution of Rochelle salt (potassium-sodium tartrate) and 50 cc. of a 10 per cent. solution of sodium bicarbonate. A little starch solution is then added and the liquid titrated with $\frac{N}{10}$ iodine until a permanent blue colour appears.

$$1 \text{ cc. of } \frac{N}{10} \text{ iodine} = .0059 \text{ grm. of Sn.}$$

Fairly good results may also be obtained by simply dissolving the

"tin crystals" in dilute hydrochloric acid and titrating direct with $\frac{N}{10}$ iodine without starch.

Indirect Estimation by Permanganate.—5 grm. is dissolved in water and hydrochloric acid. A slight excess of ferric chloride is then added, which oxidises the tin to stannic chloride, becoming itself reduced to ferrous chloride. The liquid is diluted with recently boiled and cooled water and titrated with $\frac{N}{10}$ potassium permanganate, each cc. of which corresponds to .0059 grm. of Sn.

Solutions of Stannous Chloride, containing hydrochloric acid, are sold under the names of *double muriate of tin* and *single muriate of tin*, *tin spirits*, &c. (see pp. 283, 284). The terms "double" and "single" merely refer to the density of the solutions. Single muriate varies in density from 40° to 60° Tw., and double muriate from 70° to 120° Tw. The same impurities (as well as free sulphuric acid) may be present as in tin crystals.

Estimation of Stannous Chloride.—The amount of tin present as stannous chloride may be estimated either by $\frac{N}{10}$ iodine or by ferric chloride and $\frac{N}{10}$ permanganate, as described above.

If *stannic chloride* is also present, which is frequently the case, the total amount of tin is estimated by allowing a piece of pure metallic zinc to remain in a weighed portion of the sample for 10 or 12 hours. If 25 cc. of the sample are diluted to 500 cc., 25 cc. of this solution will be a convenient amount to take. The tin, which is thus entirely precipitated in the metallic form, is carefully collected and washed, and dissolved in hydrochloric acid with the aid of platinum foil. This should be done in a flask in a current of carbon dioxide to prevent oxidation. The stannous chloride solution obtained is then titrated as above.

Estimation of Free Acid.—Since stannous chloride has an acid reaction to indicators, the free hydrochloric acid present cannot be titrated direct. In order to ascertain the amount of free acid present, it is necessary to determine the total acid (free and combined), and to calculate the amount required to combine the percentage of tin found. For this purpose W. Minor* recommends that 10 cc. of the solution be diluted with water, and the tin precipitated as sulphide by a current of hydrogen sulphide. The filtrate is made up to a litre and 500 cc. boiled, to expel H_2S , and titrated with a solution of soda. It is quite unnecessary, however, to separate the tin. The total acid may be accurately estimated by titrating the solution of stannous chloride direct with caustic soda and phenolphthalein. The stannous hydrate formed has no action whatever upon the indicator. If pure stannous chloride is titrated in this way, the exact amount of combined acid is obtained.

Example.—25 cc. of a solution of single muriate of tin = 30.83 grms. were diluted to 500 cc.

25 cc. required 21.8 cc. of $\frac{N}{10}$ iodine = 8.33 per cent. of Sn.

* *Chem. News*, vol. lxiii. (1891), p. 249, from *Zeitsch. Angew. Chemie*.

50 cc. of the diluted solution (= 3·088 sample) with phenolphthalein required 19·8 cc. of normal caustic soda.

1 cc. normal soda = ·0365 grm. of H Cl.

$$\therefore \frac{·0365 \times 19·8 \times 100}{3·088} = 23·40 \text{ per cent. of H Cl free and combined.}$$

8·33 parts of Sn require 5·15 parts of H Cl to form Sn Cl₂.

$$\therefore 23·40 - 5·15 = 18·25 \text{ per cent. of free H Cl.}$$

Analysis of Stannic Chloride.—Solutions of stannic chloride are used under various names, consisting of stannic chloride only, and of mixtures of this salt with stannous chloride (see p. 286). Acids other than hydrochloric acid, such as sulphuric, nitric, and oxalic, are also frequently present. The liquid known as *solution of tin*, sold at about 44° Tw., and containing about 8 per cent. of tin, usually consists of stannic chloride only, with a slight excess of hydrochloric acid and a little nitric acid. If any *stannous* chloride is present, a drop of the liquid will produce a white or grey precipitate with a solution of mercuric chloride.

Estimation of Tin.—The amount of tin may be determined by precipitation with zinc, as already described; or by the following gravimetric process, which gives very accurate results:—About 5 grms. of the solution are diluted with water to 200 cc., and, if any stannous salt be present, a weak solution of iodine is added until the liquid is faintly yellow. A dilute solution of ammonia is now gradually added until a faint opalescence appears, when an excess of a concentrated solution of sodium sulphate is added. The liquid is kept hot on the water-bath for one or two hours, and the somewhat voluminous precipitate washed two or three times by decantation. It is then collected on a filter, thoroughly washed, dried, ignited, and weighed as Sn O₂.

$$150 \text{ parts of Sn O}_2 = 118 \text{ parts of Sn.}$$

Free acid in solutions of stannic chloride may be estimated by caustic soda and phenolphthalein, exactly in the same way as in solutions of stannous chloride. In calculating the combined acid four equivalents of hydrochloric acid must be taken in place of two.

In addition to making a chemical analysis, tin compounds should always be examined by experimental dye-trials. The exact mode of procedure would depend upon the purpose to which the mordant was to be applied on the large scale.

COPPER COMPOUNDS.

Analysis of Copper Sulphate.—Copper sulphate, known also as *blue vitriol* and *blue stone*, crystallises with five molecules of water, Cu SO₄, 5 H₂ O. It is liable to contain *ferrous sulphate* as an impurity. Commercial sulphate of copper invariably contains small quantities of iron.

Estimation of Copper by Precipitation as CuO .—5 grm. of the sample is dissolved in about 150 cc. of water, in a porcelain basin, and heated to the boiling point. A slight excess of a solution of pure potassium or sodium hydrate is added, and the liquid gently boiled for about five minutes, when the brownish-black precipitate is allowed to subside, and the supernatant liquid poured through a small filter. Boiling water is added to the residue, and, after subsidence, the liquid is again poured off. This washing is repeated two or three times, when the whole of the precipitate is carefully transferred to the filter, and thoroughly washed with hot water. It is dried, transferred to a crucible, ignited, and weighed. The precipitate of oxide of copper should at first be ignited gently, but afterwards intensely, and weighed as soon as the crucible is cold. The ash of the filter should be ignited separately on the lid of the crucible, and any metallic copper contained therein converted into oxide by addition of a drop or two of nitric acid, and ignition. If iron is present in the sample, the precipitate will contain ferric oxide, which must be estimated and deducted (see below).

79.4 parts of copper oxide correspond to 63.4 parts of metallic copper or 249.4 parts of crystallised copper sulphate.

Estimation by Precipitation as Metallic Copper.—About .5 grm. of the sample is dissolved in a little water, in a weighed platinum dish. Sulphuric acid and a rod of pure zinc are added and the dish covered with a clock glass. The copper is thereby precipitated on the platinum. When the reaction is complete, known by a drop of the liquid producing no brown colour with sulphuretted hydrogen, the zinc is carefully removed, and the deposit thoroughly washed, dried at 100°C ., and weighed.

Instead of drying and weighing the metallic copper, it may be dissolved in a mixture of hydrochloric acid and ferric chloride (Fleitmann's method), diluted with water, and the ferrous chloride formed titrated with $\frac{N}{10}$ permanganate. There are many other volumetric processes for estimating copper, descriptions of which may be found in Sutton's *Volumetric Analysis*.

Estimation of Iron.—About 5 grms. of the sample should be taken, dissolved in 100 cc. of water and boiled with addition of a few drops of nitric acid. The liquid is cooled, diluted to about 300 cc., and an excess of ammonium hydrate added. The ferric oxide which is thus precipitated is collected on a filter, washed, redissolved in hydrochloric acid, and again precipitated by ammonia in the cold. The liquid is filtered, the oxide of iron washed, dried, ignited, and weighed.

Copper Acetate.—Copper may be determined by igniting a weighed portion of the sample, dissolving in hydrochloric acid, and treating the solution as above.

Acetic acid is best estimated by distillation with phosphoric acid (see p. 748).

ANTIMONY COMPOUNDS.

Analysis of Tartar Emetic.—This salt is largely used in cotton-dyeing and in calico-printing. It consists of the double tartrate of antimony and potassium, and contains half a molecule of water. Tartar emetic, especially if purchased in the powdered form, is liable to considerable adulteration; oxalate of antimony and the double fluoride of ammonium and antimony being most frequently used for this purpose.

Antimony as antimonious oxide may be readily estimated by titrating an alkaline solution with $\frac{N}{10}$ iodine and starch. W. B. Hart's process,* which consists in adding an excess of a solution of bleaching powder and titrating with $\frac{N}{10}$ arsenious acid, can be recommended. 0.5 grm. of the sample is dissolved in about 50 cc. of warm water and cooled. 20 cc. of a 10 per cent. solution of sodium bicarbonate and 25 cc. of a 2 per cent. solution of bleaching powder are added, and the liquid well stirred with a glass rod. If sufficient bleaching powder has been added, a drop of the liquid will now produce a blue colour with potassium iodide and starch paper. Decinormal sodium arsenite (4.95 grms. of As_2O_3 per litre) is then run in until a drop of the liquid ceases to give any coloration with the iodide and starch paper (see p. 767). The strength of the bleaching-powder solution used to oxidise the antimony is determined, when the amount of chlorine expressed in terms of arsenite is readily calculated. 1 cc. of $\frac{N}{10}$ arsenite = .006 grm. of Sb or .0072 grm. of Sb_2O_3 .

Example.—5 grm. of tartar emetic with sodium bicarbonate and 25 cc. of chloride of lime required 7.5 cc. of $\frac{N}{10}$ arsenite. 25 cc. of chloride of lime alone required 36.5 cc. of $\frac{N}{10}$ arsenite. Therefore, chlorine equivalent to 29 cc. of arsenite was used in oxidising the antimonious oxide present.

$$\therefore \frac{.0072 \times 29 \times 100}{.5} = 41.76 \text{ per cent. of } \text{Sb}_2\text{O}_3.$$

Antimony may also be accurately estimated by precipitating it as Sb_2S_3 , and weighing it as such, or distilling the sulphide in a flask with hydrochloric acid, and collecting the hydrogen sulphide evolved in a known volume of $\frac{N}{10}$ arsenite solution and estimating the excess of arsenite with thiosulphate (*Schneider*).

Pure tartar emetic contains 43.4 per cent. of Sb_2O_3 . Some samples in the market contain more than that amount, owing to the presence of ammonium antimony fluoride. If this salt is present, ammonia will be evolved on boiling with caustic soda.

Oxalate in tartar emetic may be detected and estimated, if necessary, by precipitating the antimony as sulphide in an acid solution. The filtrate is boiled to remove hydrogen sulphide, a slight excess of ammonia is then added, and the liquid made slightly acid with acetic acid, and treated with calcium chloride (see p. 749).

* *Journ. Soc. Chem. Ind.*, 1884, p. 294.

Antimony Oxalate.—The antimony in *oxalate of antimony* and other antimony salts may be determined as in tartar emetic. With salts containing antimony fluoride, however, Hart's process does not give satisfactory results. In such cases it is preferable to titrate an alkaline solution of the salt with decinormal iodine.

ARSENIC COMPOUNDS.

Arsenious acid may be examined for percentage of As_2O_3 by practically the same method as that described for standardising the $\frac{N}{10}$ arsenite solution (p. 766). 2 grms. of the sample are dissolved in water containing about 5 grms. of sodium carbonate, and diluted to 500 cc. 100 cc. (= .2 gm.) are withdrawn, neutralised with a little pure hydrochloric acid, 25 cc. of a saturated solution of sodium bicarbonate added, and the liquid titrated with $\frac{N}{10}$ iodine.

$$1 \text{ cc. } \frac{N}{10} \text{ iodine} = .00495 \text{ gm. As}_2\text{O}_3.$$

Sodium arsenate, Na_2HAsO_4 , is known as *dung salt* or *dung substitute*.

Arsenious acid, if present, is estimated by titrating a weighed amount with $\frac{N}{10}$ iodine, as above.

Arsenic Acid.—Watson Smith* recommends the following method, worked out by J. Barnes:—2 grms. of the sample are dissolved in 100 cc. of warm water, in a flask capable of holding about 500 cc.; a little sodium acetate is added to prevent any irregularity, caused by sodium chloride, which may be possibly present. A current of well-washed sulphur dioxide is now passed through the solution in excess. The liquid is then boiled until free from sulphur dioxide, allowed to cool, and diluted to 500 cc.; 50 cc. of this solution (= .2 gm. of sample) are withdrawn and mixed with 25 cc. of a saturated solution of sodium bicarbonate, and a little starch solution. The liquid is then titrated with $\frac{N}{10}$ iodine, each cc. of which is equivalent to .00575 gm. of As_2O_5 . From the percentage of As_2O_5 thus obtained the amount of arsenic, as As_2O_3 , found by direct titration, and calculated into As_2O_5 , must be deducted. If the solution is very acid, after boiling off the sulphur dioxide, it is preferable to nearly neutralise with normal sodium carbonate before adding the bicarbonate.

Sutton, in his sixth edition of *Volumetric Analysis*, states that the arsenate is not completely reduced to arsenite by operating in the manner described above, and recommends W. M'Kay's modification of Holthof's method.† M'Kay mixes the arsenate solution with 20 cc. of a saturated solution of sulphurous acid, in a bottle provided with a well-fitting, ground glass stopper, and capable of holding about 50 cc. The stopper is firmly tied down with a piece of stout cord, and the bottle then placed in a water-bath, which is kept briskly boiling for one hour. The bottle is then removed from the bath, and, when

* *Journ. Soc. Dyers and Col.*, 1884, p. 34. † *Chem. News*, vol. liii., pp. 221, 232, 243.

nearly cold, opened, and the contents rinsed into a flask, diluted to 150 cc., and concentrated to one-half. On cooling, the liquid, free from sulphur dioxide, is diluted to a known bulk, and an aliquot part titrated with iodine substantially as above. M'Kay uses $\frac{N}{40}$ iodine.

Holthof's original method consists in heating the arsenate solution with about 100 cc. of sulphurous acid and the same quantity of water for about four hours on a water-bath, and then boiling down over a free flame to one-half the original volume. M'Kay finds this mode of procedure to give accurate results, and apparently the only advantage of his modification is a saving in time. In many cases, however, where a number of samples have to be examined, heating gently for four hours may be preferred to boiling under pressure for one hour.

Arsenic Acid in sodium arsenate may also be determined by converting it into ammonium-magnesium arsenate, drying at 100° C., and weighing on a tared filter; also, by reduction as above, conversion into arsenious sulphide, and drying at 100°.

ZINC.

Analysis of Zinc Powder.—*Zinc dust, zinc preparation, or zinc powder* contains, in addition to metallic zinc, variable quantities of zinc oxide, iron, cadmium, silica, &c. It is used largely as a reducing agent, principally in the dyeing of indigo. For such purposes, therefore, its value depends entirely upon the amount of metallic zinc present.

The zinc may be determined by its action upon an excess of a standard solution of potassium bichromate. For this purpose .661 grm. of the sample (this amount of pure zinc reduces 1 grm. of $K_2Cr_2O_7$) is mixed with 80 cc. of a solution containing 25 grms. of potassium bichromate per litre and 10 cc. of dilute sulphuric acid. The same amount of dilute acid is added after 10 to 15 minutes, and repeated a third time; the liquid being stirred from time to time. 10 cc. of concentrated sulphuric acid diluted with its own volume of water are now added, followed by an excess (about 10 grms.) of pure granulated ferrous ammonium sulphate. If, after well stirring, a drop of the solution does not produce a blue colour when brought in contact with a drop of potassium ferricyanide, a further weighed amount of the ferrous ammonium sulphate must be added. The excess of ferrous salt is then determined by the standard solution of bichromate. The amount of potassium bichromate reduced by .661 of the sample multiplied by 100 gives the percentage of metallic zinc present. Any metallic iron present will, of course, also be included.

Example.—.661 grm. with 80 cc. of a solution of potassium bichromate (25 grms. of $K_2Cr_2O_7$ per litre) were subsequently treated with 10 grms. of ferrous ammonium sulphate. 6.1 cc. of the same bichromate solution were required to

oxidise the excess of ferrous iron. (1 grm. of ferrous ammonium sulphate = .1255 of $K_2Cr_2O_7$.)

$$.025 \times 86.1 = 2.1525 = \text{total } K_2Cr_2O_7.$$

$$.1255 \times 10 = 1.2550 = K_2Cr_2O_7 \text{ required by } Fe(NH_4)_2(SO_4)_2.$$

$$.8975 = K_2Cr_2O_7 \text{ reduced by zinc.}$$

$$\therefore .8975 \times 100 = 89.75 \text{ per cent. of zinc in the sample.}$$

Instead of adding such a large quantity of ferrous ammonium sulphate, the operation may be modified by diluting the solution containing the excess of potassium bichromate to a given bulk, and estimating the amount of $K_2Cr_2O_7$ still present, as given under bichromates (p. 772).

Liebschütz* takes 1 grm. of the sample, removes the iron by means of a magnet, and treats it with a warm, neutral solution of 5 grms. of copper sulphate. After standing for some time the oxides are removed by a little dilute sulphuric acid and the metallic copper well washed with water. It is then dissolved in nitric acid and the copper estimated volumetrically by titration with a standard solution of potassium cyanide. The weight of copper found multiplied by 1.032 equals the amount of zinc in the sample taken.

F. Weil† employs a standard solution of copper chloride, and after the action of the weighed sample of zinc, estimates the residual copper in solution by stannous chloride. A solution of copper chloride, containing 10 grms. of Cu per litre is prepared by dissolving 12.519 grms. of pure copper oxide (obtained by ignition of the nitrate) in a slight excess of hydrochloric acid and diluting to a litre. 50 cc. (= .5 grm. of Cu) are introduced into a porcelain or platinum capsule and dilute ammonia carefully added until the liquid becomes slightly opalescent. A weighed amount (.4 grm.) of the sample of zinc powder is now added, and a platinum wire coiled at the lower end in the form of a spiral is used to stir the mixture occasionally. When the operation is complete (known by no deposit being formed on a clean platinum wire when stirred up in the mixture) a few drops of acetic acid are added and the liquid decanted into a graduated flask holding 200 cc. The capsule and the precipitated copper are well washed with water, and the whole diluted to the 200 cc. mark and well mixed. After allowing any insoluble matter to subside, 20 cc. of the clear solution are put into a small flask, mixed with 40 cc. of pure hydrochloric acid, and titrated at a boil until completely decolorised with a solution of stannous chloride which has been standardised by the original copper solution. Deducting the copper found in solution from .5 grm., the weight of copper precipitated by the zinc in the sample is obtained. This weight multiplied by 1.032, as given above, represents the amount of metallic zinc in the portion taken for analysis.

The percentage of metallic zinc may also be determined from the

* *Journ. Amer. Chem. Soc.*, vol. vii., p. 136.

† *Chem. News*, vol. liv., p. 314.

volume of hydrogen evolved when a weighed amount of zinc powder is treated with dilute sulphuric or hydrochloric acid.

TANNIC ACID AND TANNINS.

Analysis of Tannins.—A great variety of processes have been devised for estimating tannic acid in the substances known as "*Tannins*." The majority of the published methods have had the valuation of tannins for tanning leather mainly in view, but it does not necessarily follow that these methods are equally serviceable for valuing tannins used in dyeing.

Proctor's modification of Löwenthal's process* is very generally adopted both for tanning and for dyeing purposes. The tannic acid is estimated by oxidation with a standard solution of potassium permanganate, using a known volume of a solution of indigo-sulphonic acid as an indicator. The operation is performed in two stages. In the first place the total oxidisable matters are determined, and in another portion of the solution the tannic acid is precipitated by gelatin, and the oxidisable matters other than tannin are estimated in the filtered solution. The difference between the two titrations expresses the amount of tannic acid in terms of standard permanganate. In precipitating the tannic acid by gelatin, Proctor saturates the solution with salt. Hunt† has shown that a considerable amount of gallic acid is likewise precipitated under these conditions, and recommends that the liquid be only one quarter saturated with salt. Unfortunately some of the tannic acid is thereby left in solution. Rawson has made a considerable number of experiments from a dyer's point of view, comparing the results obtained by various modifications with practical results in dyeing. His mode of working the process will be here given, although it differs but little from either Proctor's or Hunt's methods.‡

The following solutions are required:—

Standard Permanganate.—A $\frac{N}{50}$ solution of potassium permanganate is prepared by dissolving .632 grm. of the pure recrystallised salt in a litre of water. The solution is standardised by pure ferrous ammonium sulphate (p. 775), or pure oxalic acid (p. 749). Each cc. = .00126 grm. of crystallised oxalic acid.

Indigo Solution.—1 grm. of pure indigotin prepared by Fritzsche's method (p. 326) is dissolved in 50 cc. of pure concentrated sulphuric acid, and diluted with water to 1000 cc.

Gelatin Solution.—20 grms. of fine gelatin (Nelson's) are soaked in water for two or three hours, and then dissolved on the water-bath in a litre of water. The liquid is saturated with salt and filtered.

* *Journ. Soc. Chem. Ind.*, 1884, p. 82; and 1886, p. 79. † *Ibid.*, 1885, p. 263.

‡ For details of these methods, see the papers above mentioned; and for fuller particulars, also Proctor's *Text-Book of Tanning*, Allen's *Commercial Organic Analysis*, vol. iii., and Sutton's *Volumetric Analysis*.

Sulphuric Acid and Salt.—A 5 per cent. solution of sulphuric acid is saturated with sodium chloride.

Titration for Total Oxidisable Matters.—About 2 grms. of the sample (more or less according to the amount of tannin probably present) are boiled with 500 cc. of distilled water in a flask for half an hour. The liquid is quickly cooled, 5 cc. of a 10 per cent. solution of acetic acid added, and diluted to 500 cc. After shaking well, it is poured into a glass cylinder and the insoluble matter allowed to subside. [The decoction should not be filtered, since filter paper absorbs tannic acid to a considerable extent, and the amount abstracted from solution depends upon the rate of filtration.] When the insoluble matters have sufficiently subsided, which may take an hour or so, 10 cc. of the clear solution are carefully withdrawn and mixed with 500 cc. of water in a large porcelain basin, 25 cc. of the indigo solution are added, and $\frac{N}{50}$ permanganate run in from a burette in continuous drops during constant and vigorous stirring until the liquid becomes of a light green colour. The permanganate is now added more slowly until the green coloration has given place to yellow, when usually a faint, but unmistakable, pink rim may be observed. 25 cc. of the indigo solution with 500 cc. of water are titrated alone, and the number of cc. of permanganate deducted from the result. The difference expresses the total amount of oxidisable matters in 10 cc. of the decoction.

Titration of Oxidisable Matters other than Tannin.—50 cc. of the clear decoction are introduced into an 8-oz. stoppered bottle and mixed with 25 cc. of the gelatin and salt solution and 25 cc. of the acid salt solution, and well shaken. The liquid is thus practically half saturated with salt. After half an hour or so it is filtered and 40 cc. of the filtrate (= 20 cc. of the original solution) mixed with 500 cc. of water and 25 cc. of the indigo solution, and titrated with permanganate, as before. If there is a difficulty in obtaining a perfectly clear filtrate, a little kaolin or barium sulphate may be shaken up with the liquid before filtering. In the case of myrabolans and sumach, however, the filtrate is usually perfectly clear without any addition of this kind.

Example.—2 grms. of myrabolans were extracted and made up to 500 cc., as above described. 10 cc. titrated direct with 25 cc. of the indigo solution required 29.5 cc. of $\frac{N}{50}$ K Mn O₄. 25 cc. of indigo alone required 16.5 cc. of $\frac{N}{50}$ K Mn O₄.

Total oxidisable matters in 10 cc., therefore, equal to 29.2 - 16.5 = 13 cc. of $\frac{N}{50}$ K Mn O₄.

40 cc. of the filtrate from gelatin precipitate (= 20 cc. of the original solution) required with 25 cc. of indigo solution 23.2 cc. of $\frac{N}{50}$ K Mn O₄.

Oxidisable matters other than tannin in 20 cc., therefore, equal to

$$\begin{aligned} 23.2 - 17^* &= 6.2 \text{ cc. of } \frac{N}{50} \text{ K Mn O}_4. \\ &= 3.1 \text{ ,, } \text{,, } \text{ in 10 cc.} \end{aligned}$$

Therefore, 13 - 3.1 = 9.9 cc. of $\frac{N}{50}$ K Mn O₄ consumed by the tannic acid in

*.5 cc. of K Mn O₄ is here allowed for the action of oxidisable matters introduced by the gelatin. This should be determined by means of a blank experiment.

10 cc. of the infusion. The percentage of tannin is commonly expressed in terms of oxalic acid.

$$\frac{.00126 \times 9.9 \times 50 \times 100}{2} = 31.18 \text{ per cent. of tannic acid expressed as oxalic acid.}$$

According to Neubauer & Oser, .063 of oxalic acid corresponds to .04159 of gallo-tannic acid (gall-nut tannin) or .06235 of querci-tannic acid (oak-bark tannin). The percentage of tannic acid expressed in terms of oxalic acid multiplied by .666 gives, therefore, the percentage of gall-nut tannin; and multiplied by .99 the percentage of oak-bark tannin.

Commercial tannic acid and extracts of sumach, myrabolans, &c., are examined in the same manner as natural tannins, the boiling with water being omitted. About 1 grm. of tannic acid or 2 to 5 grms. of "extracts" dissolved in 500 cc. of water will give solutions of convenient strengths.

In place of gelatin, specially prepared *hide-powder* is often used to precipitate the tannin matters. 50 cc. of the decoction of tannin are treated with 3 grms. of hide-powder for a period of 18 hours (shaking occasionally) and then filtered. 10 or 20 cc. of the clear filtrate are then titrated, as above described. Concordant results are obtained, but on account of oxidisable substances other than tannin being abstracted from solution, the method cannot be recommended for dyeing purposes.

In the *Journal of Society of Chemical Industry* (1887, p. 94), Proctor describes a gravimetric process for estimating tannic acid. 50 cc. of a clear decoction of the tannin (containing about 1 per cent. of tannin) are evaporated to dryness at 100° C. and weighed. About 100 cc. of the same solution are filtered by upward filtration through a layer of 5 grms. of hide-powder contained in a glass tube. 50 cc. of this filtrate deprived of its tannin are evaporated under the same conditions and weighed. The difference between the two results represents the amount of tannin in 50 cc. Gallic acid and other bodies of no value in dyeing, however, are likewise partially withdrawn from solution, and, therefore, for dyeing purposes the same objections are attached to the process as in the volumetric method where hide-powder is used.

The *Journal of the Society of Dyers and Colourists* (1888, p. 62) contains a description of a method, by Collin & Benoist, of estimating tannic acid by means of a standard solution of gelatin sterilised by a small quantity of mercuric iodide. They use methylene-blue (in some cases alkali-blue) as an indicator, and operate in the presence of calcium acetate. In the description given very strong solutions are recommended, and 1 cc. only of gelatin is taken for the titration. The solution of tannic acid used for standardising the gelatin is made to contain 5 grms. of the pure dry acid per litre, and of this solution only about 3 cc. are required. Consequently $\frac{1}{10}$ of a cc. corresponds to an error of ± 3 per cent. Collin & Benoist use, however, special burettes

constructed to give at least four drops to the tenth of a cubic centimetre.

Examination of Tannins by Dye-trials.—Whatever method of analysis is used for estimating tannic acid, the results should always be confirmed by making experimental dye-tests. The exact mode of procedure may vary according to the kind of tannin under examination and the uses to which it is to be put, but the following can be recommended for general purposes:—2 grms. of each sample (myrabolans, sumach, &c.) are boiled for fifteen minutes with half a litre of water. The decoctions (with insoluble portion) are made up exactly to 500 cc., and poured into beakers, which are then introduced into a steam bath as described below. 10 grms. of common salt are added to each beaker, and when the temperature is uniform (about 95°), 10 grms. of cotton yarn (previously thoroughly wetted) are introduced. The yarn is worked on glass rods dipping beneath the surface of the liquid, and the solutions allowed gradually to cool. After three hours (or more) the yarn is taken out and the excess of liquid removed (not washed), and each hank introduced into separate beakers, containing 200 cc. of basic ferric sulphate (nitrate of iron), of specific gravity 1.01 (2° Tw.). After 15 to 20 minutes the yarn is taken out, washed, dried, and the depth of shade compared. It is most important that in each series of tests, the conditions as to temperature, time, amount of water used, &c., should be exactly the same for each sample.

EXAMINATION AND ANALYSIS OF DYES.

Comparative Dye-tests.—Generally speaking, the most satisfactory method of valuing dyes is by means of carefully conducted experimental dye-trials. It is most important that the tests be made under identical conditions, since, in many cases, a slight variation in temperature or volume of water used causes a considerable difference in the results. A convenient form of apparatus consists simply of a rectangular copper vessel, measuring about 18 ins. long, 12 ins. wide, and 8 ins. deep. Six circular holes, about 4½ ins. diameter, are cut out of the top to receive the dye vessels. These are preferably glass beakers of about a litre capacity, which fit into the copper vessel resting on india-rubber rings. The vessels (beakers) should be as nearly as possible of the same size. They are heated by means of steam, evolved from water kept briskly boiling in the copper bath. A slightly higher temperature in the dye vessels may be attained by adding common salt, or some other salt, to the water in the copper bath; but for all ordinary purposes where glass beakers are used no addition is required. Fletcher's tube-burner, No. B 24, is recommended for boiling the water in the copper bath.

Sometimes earthenware pots are used in place of glass beakers, but on account of the thickness of the vessels it becomes necessary to

use either strong saline solutions, oil or glycerin in the copper bath. The water in the dye-pots, however, does not usually get heated regularly, and in order to overcome this difficulty, as well as to reduce the risk of fire attendant on the use of an ordinary oil bath, R. L. Whiteley* has devised an improved bath, which is shown in Fig. 110.

It is made in two parts. The lower portion (a), made of copper welded and brazed together, measures $21\frac{1}{4}$ in. \times $15\frac{1}{2}$ in. \times 6 in. and has

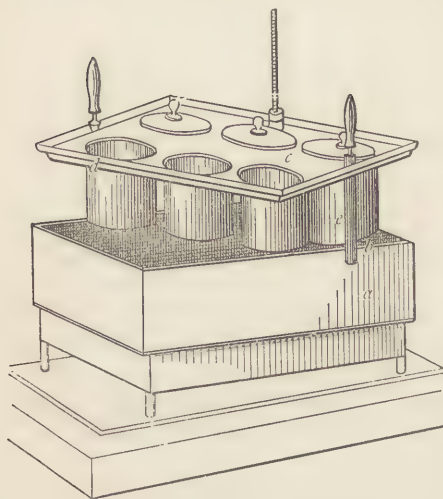


Fig. 110.—Whiteley's oil-bath for dye-testing.

an internally-projecting rim, b, so that in case the temperature should rise to the boiling point of the oil, it will be thrown towards the centre. The upper portion of the bath, c, fits into the lower by means of the rim, d, which projects downwards about $\frac{3}{4}$ in. In this portion, which is tray-shaped, six copper cups (5 in. deep and $5\frac{1}{2}$ in. wide) are fixed to receive the dye-pots. The space between the dye-pot and the cup is filled with glycerin. The tray is provided with an aperture for a thermometer, and at each end projects a handle by

means of which the flaps, e, can be moved and the oil stirred so as to equalise the temperature. Cotton-seed oil is recommended to be used for the copper bath, which is heated to a temperature of 160° to 170° C. by means of a set of three Wright's No. 310 burners.

An arrangement for heating dye-pots by means of steam, patented by D. Dawson and H. Broadbent, is described in the *Journ. of the Soc.*

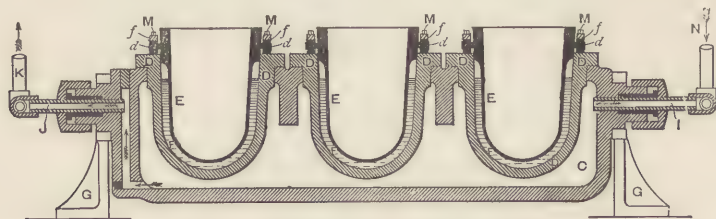



Fig. 111.—Experimental dyeing apparatus.

Dyers and Colourists, 1885, p. 287. The apparatus is in use in the dye-house of the Yorkshire College and in many other dyeing schools.

* *Journ. Soc. Chem. Ind.*, 1891, p. 521.

Fig. 111 represents a longitudinal section of the apparatus; C are metal boxes or vessels having cavities or openings in the top, in which are screwed (or otherwise fastened, so as to be steam-tight) metal pans, D, which receive the dye-pots, E, leaving an annular space, F, between the pan and the pot, which space is filled with glycerin, oil, or other suitable liquid. The box, C, which carries the dye-pots is supported at each end by suitable standards, G, and is made with a stuffing-box axis, so as to be capable of being turned over for the purpose of emptying the contents of the dye-pots. Steam to heat the glycerin enters at the part, N, and passes through the pipe, I, into the box, C, whereby the pans, D, and their contents are heated; the steam and condensed water then make their escape through an outlet, near the bottom of the box, C, through the pipe, J, and finally out at the point, K.

This apparatus, although exceedingly convenient for experimental dyeing of various kinds, is not altogether satisfactory for valuing dyes, since the temperature of the water in the several dye-pots does not invariably rise in a uniform manner. Perhaps the best method of working with this apparatus is to pour the same quantity of water into each pot (about half-full), and pass the steam until the water in each vessel boils. Then fill up quickly with cold water, and have the necessary materials ready to enter into the several baths.

In making experimental dye-tests the amount of dye used in comparison with the material to be dyed must be small—not nearly sufficient to produce what may be termed a full shade. In the first place, it is difficult to discriminate between deep shades of colour; and, again, if too much dye be used, much of it may be left in the baths, and probably in unequal quantities. The material to be dyed is best suspended in the vessel by means of a glass-rod bent thus—. The yarn or cloth, quite free from oil and other impurities is previously thoroughly wetted out, so as to guard against unevenness, and frequently and regularly turned, by means of a straight glass-rod, during the course of one to two hours, as circumstances require. The exact mode of procedure varies, of course, according to the properties of the colouring matters to be examined, and the purposes to which they are to be applied. As a rule, the method employed should be similar to that which is followed on the large scale, although, in certain cases, slight modifications may be introduced with advantage. In testing dyewoods, alizarin colours, and other colours for which mordants are required, for example, it is preferable to use rather a larger proportion of the mordant than would be found necessary to dye a good shade on the large scale. The material to be used in making the dye-trials depends, to a certain extent, upon the application of the colouring matters under examination. The woollen-dyer may use either slubbing, yarn, or cloth, but, for most purposes, fine botany yarn will be found most convenient. Even the cotton-

dyeer may frequently find it advantageous to make his dye-tests upon worsted yarn, since many colouring matters which may be applied to the dyeing of either wool or cotton are taken up by the wool fibre much more completely, and, consequently, less colour is left in the bath. It is most important that the dye-bath should be exhausted as completely as possible, otherwise more colour may be left in solution in one case than in another. Many of the dyestuffs are taken up by wool and silk so completely that the dye-bath is quite colourless. Other colouring matters, however, cannot be completely withdrawn from their solutions in this manner, and, in such cases, it is necessary to dye a second, and perhaps even a third lot of material without a further addition of colour. Among the dyes which are not easily withdrawn from solution may be mentioned picric acid, malachite-green, alkali-blue, archil and cudbear, and vat-indigo.

For the dye vessels which have been already mentioned (1 litre capacity), 10 grms. of worsted yarn or cloth, or 20 grms. of cotton yarn, will be found a convenient quantity, but in the case of cotton dyeing it is preferable for the sake of uniformity to employ vessels of 500 cc. capacity, and to dye 10 grms. In the case of coal-tar colours about 0.5 per cent. (varying according to circumstances) of the dye, calculated on the weight of the material, should be used. The requisite amount of colouring matter should not be weighed out direct and added to the dye-baths, but standard solutions should be made by dissolving 1 gm. of each sample in a litre of water. Each cc. of such a solution would contain 1 milligramme of colour, and, consequently, 100 cc. on 10 grms. of material would correspond to 1 per cent.

If it be required to ascertain which is the cheapest of two or more samples of dyes of a similar kind, the simplest plan is to dye equal weights of material with quantities in inverse proportion to their prices. For example, supposing that three samples of azo-scarlets at $1/0\frac{1}{2}$, $1/3$, and $1/8$ per lb., respectively, are to be examined. Three lots of yarn, each weighing 10 grms., are dyed respectively with 0.8 per cent. of the first sample at $1/0\frac{1}{2}$ per lb., 0.66 per cent. of the second at $1/3$ per lb., and 0.5 per cent. of the third at $1/8$ per lb. These quantities represent equal money values, and, therefore, that swatch or hank which comes out the best in the dye-trials will be the cheapest. It might be mentioned here that in dyeing such colours as azo-scarlets, $2\frac{1}{2}$ per cent. of sulphuric acid and 10 per cent. of sulphate of soda should be added to each bath. If the relative value of two or more samples of colouring matter be required, the problem is not quite so simple. In the first place, equal quantities of material—wool, cotton, or silk, as the case may be—are dyed respectively with equal weights of the various samples. After washing and drying, the swatches or hanks are compared, and a second series of tests made, using a greater quantity of those samples which produced lighter shades, or less of those which gave deep shades, according to what is judged will be

sufficient to yield the same depth of shade in all cases. It will generally be found necessary to make three, or perhaps four, series of tests in this way. It is sometimes recommended to attain this end in one series of tests, by adding more colouring matter from time to time, as occasion requires, to those baths which produce lighter "shades" and by continuing the dyeing until all the patterns have acquired the proper degree of saturation and appear of the same shade. This plan, although occupying considerably less time, does not give such reliable and satisfactory results as the process which has been already described. The relative value of the samples will be in the inverse proportion of the amount of dye required to produce the same shade. For example, if with two samples of magenta, 56 cc. of one produced the same depth of shade as 70 cc. of the other, their relative value would be as 70 : 56, or expressed centesimally as 100 : 80. It must be borne in mind that such valuations are only strictly accurate when the various samples under examination are of the same tone; a pure bright colour being more valuable, of course, than a dull one. In the case of rosaniline-blue, for instance, the red shades are not so valuable as the pure or greenish shades of blue. Artificial light is of great service in comparing many shades, especially for green, blue, and violet, since by these means certain peculiarities are brought out very distinctly. Thus, a blue with a slight cast of red appears almost violet in gas or candle light, while a blue with a slight shade of green appears distinctly bluish-green. Whenever a fresh lot of dye requires comparing with an old standard, it is always necessary to make a dye-trial of that standard *at the same time*, for, however careful one may be to work under the same conditions, dye-tests made at different times with the same sample may vary slightly in character. From what has been previously stated, it is scarcely necessary to mention that in testing those colouring matters which require mordants, the cloth or yarn must be prepared in a similar manner to that which is dyed on the large scale. It is of great importance that the cloth or yarn should have been mordanted at the same time and under identical conditions—preferably in one bath. In all cases the material used—cotton, wool, or silk—should be of exactly the same quality for each series of tests.

Colorimetry.—In certain cases, the relative value of dyes may be ascertained by making colorimetric observations of their solutions, but the results cannot be considered as reliable and satisfactory as comparative dye-trials. The impurities present in many dye-wares render the observations somewhat difficult and obscure. Whilst many of the coal-tar colours may be estimated fairly accurately by "colour titration," others—especially yellows, oranges, and scarlets—do not always give results which are confirmed by dyeing. In other words, two colours may give a similar shade and depth of tint in solution, and produce very different effects in dyeing, and *vice versa*. A good colorimeter, however, will be found very useful in the examination

of dyes as a preliminary step, or in some cases as a check upon the dye-tests.

There are various forms of apparatus designed for this purpose, and the methods of working differ to some extent, but the principle is the same in all cases. A simple and useful instrument consists of two graduated Nessler tubes, each being provided with a stopcock near the base. The solutions to be examined must be very dilute, otherwise it will be found impossible to discriminate between a small difference of intensity of two solutions. In the case of pure coal-tar colours, the solutions to be used for 100 cc. cylinders, should contain only 2 to 5 milligrammes of colouring matter per litre. In examining two solutions, 100 cc. of each are placed in the Nessler glasses, and, on looking through the liquids downwards, if one appears darker than the other, a little is carefully run off until the two solutions appear of the same intensity. The volume of the liquid in each tube is observed, and the figures will denote the inverse ratio of the value of the two samples. Suppose, for example, that equal weights of two samples of magenta were dissolved in equal volumes of water, and that 75 cc. of the one gave the same depth of colour as 100 cc. of the other, the relative value of the two samples would be as 100 : 75. It will, of course, be understood that the two cylinders or Nessler glasses must be of the same diameter throughout their entire length. The ordinary plain Nessler tube may be used for the same purpose in the following manner:—Solutions of the dyes are made of about ten times the strength of those above mentioned. In the case of magenta, &c., 50 milligrammes per litre will be found a convenient strength. Having prepared the solutions, 10 cc. of the standard are run into a Nessler glass and diluted with distilled water to the mark (100 cc.), and more or less of the other solution is measured into a second glass, diluted in a similar manner, until the same depth of colour is reached in both tubes. The relative value of the two samples will be in inverse proportion to the number of cc. required.

The colorimeter devised by Dr. Mills (Fig. 112) can be highly recommended for all purposes of colour titration. It is described in Sutton's *Handbook of Volumetric Analysis* as follows:—"Mill's detached colorimeter is made in two pieces, alike in every respect; one of these is represented in the subjoined figure. It consists of a stout glass tube having a broad flat foot, and graduated into 100 equal parts; its capacity is about 120 cc. On the top of this is a loosely fitting brass cap, prolonged downwards, so as to cover and shade the surface of the liquid, thereby preventing the appearance of a dark meniscus. The surface of the liquid is only visible sideways through the little aperture cut for that purpose. The cap is perforated centrally; and a short tube rises from the perforation. This tube is soldered laterally to a narrower one, and this again to a small block, from which rises a spring carrying another small block. The narrower tube has cemented

to it a glass tube, which passes straight downwards, and reappears below the flat surface of the cap, its end amply clearing that surface. This tube is coned outwards at its upper extremity, but is left plain below. Through it there passes, with just sufficient room to move, a rod, bent below twice at right angles, so as to carry a flat circular opal glass disc, to which it is attached by fusion. These discs are turned in the lathe; their surfaces should be polished free from scratches, and their edges show no bevel. The rod is prevented from slipping by the easy pressure of a little half-tube, carried by a small block. When the thumb and forefinger are lightly pressed on each side of the cap, the rod can be easily moved up and down, and will then stay in any position in which it may have been left. It is convenient to cone outwards the half-tube at both its ends, but only traces of liquid ever reach this spot. The instrument has two accessories which are of considerable service. These consist (1) of a pair of glass discs, lying at the bottom of the tube, one having a suitable red, the other a green colour; there is thus obtained a black background on which the opal disc is always seen through the upper opening.

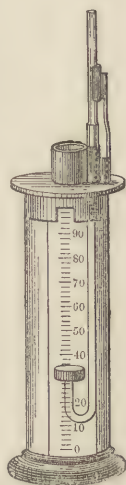


Fig. 112.—Mills' colorimeter.

An annulus of a deeper tint than a given observed colour, would otherwise surround the opal disc, and tend to confuse the determination. It is an advantage at times to use other colours, and even to cover the opal disc with a plate of coloured glass. The other accessory is (2) a black hemispherical button which lies loosely on the opal disc. It is used in the estimation of turbidities, by lowering it until it just disappears from view. In taking readings, the position of the flat surface with regard to the scale, is always the object to be ascertained; and this can be done, as is the case with Erdmann's float, so as entirely to avoid parallax. The level of the liquid's surface is afterwards taken; and the difference between the two readings is the depth required. It is obvious that any upward or downward movement of the rod must alter somewhat the level of the surface of the liquid. For small variations thus produced, no correction need be made; for larger variations a factor is easily found by experiment. It is probably the same in every specimen of the instrument—viz., 0.015 division for every division the rod is moved. In using the instrument, the two coloured discs are put in first. The cap is then placed on one of the tubes, and the piston pushed down as far as it will go, the little window being over the scale. A clear coloured solution of known strength is poured in through the brass tube at the top, until the mark 100 is exactly reached. The other tube is similarly filled with a solution of the sample to be compared and placed beside the first. The pistons are now raised until when observed with the same eye,

the depth of tint in both tubes appears to be the same. The scales are then read, and the relative strength of the two solutions are inversely as the numbers of divisions."

In connection with this subject, the **Tintometer**, a new instrument for the analysis, synthesis, matching, and measurement of colour, devised by J. W. Lovibond,* might be mentioned here. The instrument not only serves the purpose of a colorimeter, but also of a colour recorder. The apparatus, apart from stands and reflectors, may be divided into two essential parts; the first is an instrument giving two fields of view under exactly similar monocular conditions, freed from the errors arising from unequal side lights, and the different power of distinguishing which may exist in the eyes of the observer. The second part consists of standard sets of coloured glass slips, the glasses composing each set being all of the same colour, but regularly graded for depth of tint; each series of one colour bearing a denominational or "colour number;" the depth of tint being also noted on the slips by an additional "tint number" engraved on the slip below the colour number. The use of several superimposed glasses from a single set produces a depth of tint represented by the aggregate of tint numbers on the glasses used, while glasses from several sets produce a composite colour, and the exact proportion of each colour can be read off.

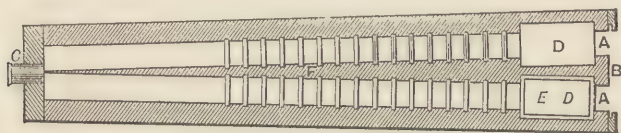


Fig. 113.—Lovibond's tintometer.

The instrument consists of a tube divided by a central partition, F B (Fig. 113), terminating at the eyepiece, C, in a knife-edge, which, being inside the range of vision, is not seen when the instrument is in use. At the other end of the instrument are two receptacles, D, D, of equal value, alterable in size and shape by means of diaphragms. The two receptacles are here divided by the thick end of the partition, B, which, together with the sides, is recessed by grooves in order to hide the edges of the standard glasses and of the vessels placed in the tube for observation; the top is provided with slots in line with the grooves, which admit and guide the coloured standard glasses into the tubes. A friction rod with clips is fitted on each side to retain the vessels of liquid in position, and the whole is arranged in such a way that the only light which can reach the eye of the observer must first pass in equal quantities through the object in one tube, and the standard glasses in the other.

For measuring colour in opaque objects the instrument is fitted to a

* *Journ. Soc. Dyers and Col.*, 1887, p. 186.

hinged stand, capable of being placed at such an angle as reflects the light from the whitened bottom and sides through the tubes to the eye, so that on looking through the eyepiece two white equal fields of view are seen; the object to be measured is placed on the stage under one tube, and the standard glasses worked in the other, against the white back ground. When the colour of two objects are to be compared with each other, one is placed under each tube, and standard glasses added to the lightest in colour until both sides are equal, when the difference between them, either in depth of colour or tint, can be read off.

The vessels for holding liquids to be measured are gauged to contain a body of liquid varying in thickness from $\frac{1}{16}$ in. for dark liquids, up to 2 feet for very pale liquids; with the latter the depth of the blue colour of distilled water can be easily measured. The vessels are made in brass, with colourless glass ends, for neutral and alkaline solutions, and entirely in glass for acids and other corrosive liquids.

When dissimilar substances are to be compared or measured, the intensity of light used becomes an important factor, and extremes cannot be ignored, for whilst there is a considerable range of daylight within which the judgments of the eye are uniform, care is required outside these limits, and practice soon shows at what point the work must be abandoned from insufficient light; and with a light-growing intensity, where the use of modifiers should begin. In matching a given colour, it is found best to make a mental estimation of the primary colours of which the sample is composed, and, if possible, match entirely by means of primaries; but as primaries in glass are at present unsuitable, it sometimes becomes necessary to start with the compound standard colour which nearest approaches that under examination, and finish the matching with the primaries in which it may be deficient.

From the description already given, it will be seen that when either a liquid or a solid colour has been matched with the standards, the numbers on the matching glasses afford a complete record of the several colours and tint units of each colour constituting the shade matched. In testing colouring matters, the samples are dissolved in water, alcohol, or other liquid, as the case may require; one of the gauged glass vessels is filled with the solution and placed in position (as shown at E D) on one side of the instrument, and the colour compared either with the standard glasses or with a solution of a standard colour. As previously stated, it is most important that the colour should not be too deep. The best matchings are made with colours equal in depth to 10 or 20 tint units; if much deeper than this, the solution should either be diluted or a gauged glass of less thickness be employed.

The tintometer will be found of especial value to the colour and extract manufacturer, and wherever colouring matters have to be brought to a given standard of strength or shade.

INDIGO.

During the past few years the analysis of this most important and valuable dyestuff has received considerable attention from chemists both in Europe and America. Notwithstanding the fact that commercial indigo varies in value from about 6d. to 7s. per lb. (usually from 3s. to 5s.) it was, until comparatively recently, almost universally bought and sold by mere inspection only, or by the application of a few rough tests, for the most part utterly untrustworthy. Even at the present day indigo to the value of many thousands of pounds annually changes hands without any pretence at analysis. And yet two samples of indigo having a similar appearance, may vary in actual dyeing value to the extent of 20 to 30 per cent. It is true that, with certain classes of indigo, brokers and dealers after long experience are able to judge the value with astonishing accuracy, yet in numerous cases their estimations have been known to be in error to the extent of 3d. to 9d. per lb. No doubt the reason that such a valuable colouring matter as indigo has not long ago been bought and sold on the results of analysis is in a great measure due to a want of confidence dyers have in chemical analysis generally. And considering the numerous rough-and-ready methods of testing dyes, which have been from time to time recommended, it is not surprising that a more scientific mode of buying indigo should not universally prevail. Methods of analysis have been used which are probably more misleading and more liable to error than even buying "at sight." But surely, with such a valuable material as indigo, it should not be thought desirable on the score of rapidity to substitute a doubtful process for one of accuracy and reliability which may possibly take a little longer time to perform. Methods of analysis, however, have been greatly improved, and a reaction is now taking place. Much indigo is now bought on the percentage of colouring matter which it contains, and probably before many years this custom will generally prevail, just as soda ash and bleaching powder are bought and sold according to the percentage of alkali and available chlorine they respectively contain.

The value of dyes as a class is ascertained by making comparative dye-trials. It is only in a few cases that methods of chemical analysis are used. Indigo stands out prominently as one of these exceptions. Unless the colouring matter in a dyestuff can be readily determined with a fair degree of accuracy, the method of valuing by comparative dye-trials is much to be preferred. It should be borne in mind, however, that the experimental error involved in making dye-tests is great in comparison with that of an ordinary chemical analysis. Let the conditions be ever so favourable, the eye is incapable of discriminating

between two shades of the same colour if the difference is less than a certain small amount, which in a chemical analysis would be considered great.

It has often been recommended to test samples of indigo by means of dye-trials in small vats in a similar manner to the dyeing of indigo on a large scale; the zinc or hyposulphite vat being the one usually recommended. The results, however, are altogether untrustworthy. It is impossible to secure identical conditions in the several small vats employed, and the slightest variation is sufficient to cause a great difference in the depth of shade obtained. Two tests made with the same quantity of the same sample rarely come out the same; very often the difference is great. A much better method of making dye-trials with indigo and one which gives fairly good results, is to dye swatches of woollen cloth or yarn with the indigo disulphonic acid. For this purpose 0.5 gm. of the sample is dissolved in 20 cc. of concentrated sulphuric acid and diluted with water to 500 cc. 10 grms. of wool are then dyed with 50 cc. of this solution and compared at the same time with a standard sample. Fairly good results may be obtained by making colorimetric tests with these solutions, which, however, must be filtered from the dark green insoluble matter usually present. But even after filtering, solutions obtained from various indigos often possess very different shades on account of varying quantities of impurities present, and, when this is the case, it is very difficult to arrive at satisfactory results. This difficulty, however, may be removed by precipitating the colouring matter with salt and redissolving it in distilled water.

In the *Journal of the Society of Dyers and Colourists* (vol. i., pp. 74 and 211), Rawson gives a description of various methods of Indigo-testing,* and classifies the processes into three groups.

I. Where the indigo is dissolved in concentrated sulphuric acid.

(a) Oxidation processes. (b) Reduction processes.

II. Where the indigotin is estimated by sublimation.

III. Where the indigo is reduced to indigo white in an alkaline solution; the indigotin reoxidised, separated, purified, and weighed.

I. Solution in Sulphuric Acid.—In the first place, it is, of course, important that the sample taken for analysis should represent as nearly as possible the bulk from which it has been obtained. This is best performed by taking small pieces from each of the lumps in the sample and pounding them together in a mortar. After grinding a portion to an impalpable powder, it is passed through a fine sieve, and any particles remaining are returned to the mortar, until the whole is fine enough to pass through the sieve.

Regarding the solubility of indigo in sulphuric acid, writers differ

* See also Helen Cooley, *Journ. Anal. Chemistry*, vol. ii., p. 129; E. v. Cochenshausen, *Leipziger Monat. für Textil-Industrie*, vol. iii., p. 406; F. Ulzer, *Mitth. des k. k. Technol. Gewerbe-Museums*—abstract in *Journ. of Soc. Dyers and Col.*, 1891, p. 183.

very greatly; not only in respect to temperature and time to which the mixture is to be exposed, but also as to the quantity and strength of acid to be employed.

The following method of dissolving the indigo has been found to give the most satisfactory results:—

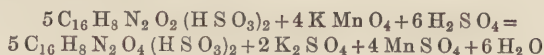
Half a gramme of finely-powdered indigo is intimately mixed in a small mortar with its own weight of ground glass. The mixture is gradually and carefully added, during constant stirring with a glass rod, to 20 cc. of concentrated sulphuric acid (sp. gr. 1.845) contained in a cylindrical porcelain crucible (cap. $1\frac{1}{2}$ oz.); the mortar is rinsed out with a little powdered glass, which is added to the contents of the crucible, and the whole is exposed in a water oven for a period of $\frac{3}{4}$ to 1 hour to a temperature of about 90° C. The sulphindigotic acid thus formed is diluted with water, made up to 500 cc., and the liquid filtered in order to separate certain insoluble impurities, which would otherwise interfere with subsequent operations.

Pure indigo blue dissolved in sulphuric acid is, by the action of various oxidising agents, more or less readily converted into a pale yellow body named sulphisatic acid. The substances which have been most generally used for the purpose of analysis are chlorine, bichromate of potash, and permanganate of potash. Unfortunately all these bodies attack, not only the indigotin, but also the green and brown substances which are present to a greater or less extent in samples of commercial indigoes. When, therefore, an analysis is made by the employment of a standard solution of chlorine, bichromate of potash, or permanganate of potash, the result obtained is always too high, and, as a rule, the poorer the quality of indigo the greater will be the error, on account of the presence of larger quantities of other substances possessing no tinctorial power.

(a) Potassium Permanganate Method.—Of all the processes depending upon the oxidation of indigo this is by far the best. It is important (as it is in all other cases) to operate upon very dilute solutions, otherwise the end of the reaction is obscured by the dark colour of the liquid. This fact has been overlooked by previous writers, and has been the cause of bringing the permanganate method, along with other oxidation processes, into disrepute.

The following mode of procedure is recommended:—25 cc. or 50 cc. of the filtered solution (prepared as above described) are measured into a porcelain dish, to which are added 250 cc. of distilled water. To this diluted liquid a solution of $\frac{N}{50}$ permanganate of potash (.632 grm. per litre) is gradually run in from a burette until the liquid, which at first takes a greenish tint, changes to a light yellow. With indigotin and the better qualities of indigo the end of the reaction is remarkably clear and distinct, and even with an inferior "Kurpah" containing much foreign matter it is easy, with a little practice, to obtain results agreeing very closely one with another.

According to the equation—



four molecules of potassium permanganate oxidise five molecules of sulphindigotic acid, and consequently 316 parts of potassium permanganate become the measure for 655 parts of indigotin. Although with a strong solution of indigotin the theoretical quantity of permanganate is decolorised, yet it has been found, on working with a dilute solution, that the end of the titration is reached by the consumption of a smaller amount of potassium permanganate than is indicated by the above equation. In order to obtain comparative results it is necessary that the solution of indigo should be dilute, in which case the reaction which takes place is not strictly according to the above equation; therefore the strength of the "permanganate" solution should be ascertained by dissolving .5 grm. of pure indigotin in sulphuric acid, and treating the solution obtained as previously described. With the dilution given above, each cc. of $\frac{N}{50}$ potassium permanganate corresponds to 0.0015 of indigotin. The results obtained by this method are somewhat too high, yet they give one a fairly approximate idea of the relative values of different samples under examination.

Action of Potassium Permanganate upon Indigo-Gluten, Indigo-Brown, and Indigo-Red.—Twenty grammes of a medium quality of indigo were successively treated with hydrochloric acid, sodium hydrate, and alcohol. These extracts were separately evaporated to dryness, and a weighed portion of each treated with concentrated sulphuric acid, and afterwards diluted with water and filtered. The filtered solution in each case was mixed with 50 cc. of a standard solution of pure indigo-sulphate, and titrated with potassium permanganate. The "alcoholic extract," consisting principally of indigo-red, dissolved in sulphuric acid with a dark crimson colour, but, on the addition of water, a brown precipitate formed, showing that some indigo-brown was also present in the extract. Indigo-red was found to be acted upon by "permanganate" to the same extent as indigotin, but the oxidation takes place much more slowly. In a mixture of indigotin and indigo-red, the former body is entirely decolorised by potassium permanganate before the indigo-red is affected. On continuing the addition of permanganate the crimson solution gradually becomes yellow, passing through various shades of scarlet and orange. The "sodium-hydrate extract," consisting of indigo-brown, dissolved in sulphuric acid with a deep dark-brown colour, but, on the addition of water, it was almost entirely precipitated. The filtered solution had very little action upon potassium permanganate. The "hydrochloric acid extract" contains indigo-gluten, resinous substances, mineral matter, &c. The solution decolorised a considerable amount of permanganate, which was found to vary in quantity, according to the quality of the indigo from which the extract had been prepared.

Much of this decolorising action was found to be due to the presence of iron in the ferrous state. Indigo-red can scarcely be considered an impurity of indigo, and as indigo-brown does not sensibly affect the results, it is evident that the inaccuracy of the permanganate method is due to the presence of substances soluble in hydrochloric acid.

Improved Permanganate Method.—In order to eliminate the error due to the oxidising action of permanganate upon substances other than indigotin, the colouring matter is precipitated by common salt, and the extraneous matter removed by filtration. The 50 cc. of the filtered solution of indigo, instead of being directly titrated with permanganate, are mixed in a small flask or bottle with 50 cc. of water and 32 grms. of common salt. The liquid which is thus almost saturated with salt is allowed to stand for an hour, when it is filtered, and the precipitate washed with about 50 cc. of a solution of salt (sp. gr. 1.2). The precipitated sulphindigotate of soda is dissolved in hot water, the solution cooled, mixed with 1 cc. of sulphuric acid, and diluted to 300 cc. The liquid is then titrated with potassium permanganate as before. It is necessary to make a slight correction in order to allow for the small quantity of sodium sulphindigotate which dissolves in a saturated solution of common salt. This correction for the quantities given has been found to be .001 gm. If the indigo previous to its solution in sulphuric acid is treated with strong hydrochloric acid, washed well with water and dried, it is unnecessary to precipitate the colouring matter with salt.

Calculation of results :—

Example 1.—By direct titration—

(1 cc. of potassium permanganate = .0015 gm. of indigotin). 1 gm. of "Kurpah" indigo was dissolved in sulphuric acid, diluted to a litre and filtered; 25 cc. (= .025 of indigo) diluted with 250 cc. of water required 8.3 cc. of permanganate;

$$\therefore \frac{.0015 \times 8.3 \times 100}{.025} = 49.80 \text{ per cent. of indigotin.}$$

Example 2.—After precipitation by sodium chloride—

50 cc. (= .05 gm. of indigo) of the above solution were mixed with 50 cc. of water, and 32 grms. of common salt. The precipitate was collected on a filter, and dissolved in 300 cc. of water containing 1 cc. of sulphuric acid. This solution required 15.2 cc. of permanganate;

$$\therefore \frac{(.0015 \times 15.2 + .001) \times 100}{.05} = 47.60 \text{ per cent. of indigotin.}$$

Potassium Ferricyanide Process.—This method, which was recommended by Ullgren, may be found fully described in the *Journal of the Chemical Society*, 1865, p. 223. It is based upon the fact that potassium ferricyanide (red prussiate of potash) in the presence of free alkali changes indigo-blue into isatin. Ullgren says that the quantity of sulphuric acid employed for dissolving the indigo must not be more than ten times the weight of the indigo taken, and that the mixture should not be exposed to a temperature exceeding 50°. When 1 gm. of indigo has been dissolved and diluted to 1 litre, 10 cc. are taken

and mixed with 20 cc. of a cold saturated solution of sodium carbonate, and 1 litre of distilled water in a porcelain basin; a weak solution of potassium ferricyanide (2.5115 to a litre) is gradually added during constant stirring with a glass rod. The impurities present in commercial indigos do not so much interfere with this reaction as in the methods previously mentioned, still the results obtained are too high, and, furthermore, as both the solution of indigo and that of the ferricyanide must necessarily be very dilute, the end of the reaction is not sharp, and consequently analyses made with the same sample of indigo do not agree so well as those obtained by the permanganate method.

(b) *Hyposulphite Method.*—This process, which was recommended by A. Müller,* depends upon the fact, that a solution of sodium hyposulphite (NaHSO_2) reduces disulphindigotic acid quantitatively to disulpho-leucindigotic acid. The apparatus required for this operation is rather elaborate, and considerable care must be exercised in its manipulation; but when all the details are carried out, analyses may be performed in a short space of time, with very great accuracy. The mode of procedure given in the following differs somewhat from Müller's description, but only in a few details.

Preparation of Sodium Hyposulphite.—A flask of about 100 cc. capacity, is loosely filled with twisted sheet zinc, and this is covered with a solution of sodium bisulphite (sp. gr. 1.30). The flask is corked, and allowed to stand for about an hour, when the solution will be found to have lost the smell of sulphurous acid. The liquid is now decanted, and well mixed in a large flask or bottle, with 5 litres of distilled water, containing in suspension about 50 grms. of recently slaked lime. The vessel is closed to prevent access of air, and, after allowing the insoluble matters to subside, the clear liquid is syphoned off into a convenient store bottle, and about 100 cc. of petroleum oil are poured on the surface of the liquid to prevent oxidation. The bottle is provided with a cork through which pass two tubes, one of which is in the form of a syphon, and is used to fill the burette; the other tube, which only just passes through the cork, is connected with a supply of coal-gas or hydrogen. The strength of the hyposulphite solution is further preserved by covering the bottle with a sheet of black paper.

Standardising the Hyposulphite.—The solution may be standardised either by pure indigotin, or by an ammoniacal solution of sulphate of copper, using in the latter case a solution of indigo-carmin as an indicator. Bernthsen pointed out in 1881† that ammoniacal sulphate of copper alone could not be used for estimating the strength of a solution of sodium hyposulphite, as the solution of sulphate of copper became colourless before it was completely reduced. On this account he proposed that, towards the end of the titration, a few drops of

* *American Chemist*, v., p. 128.

† *Berl. Berichte*, vol. xiii., p. 2277; *Chemical News*, vol. xliii. (1881), p. 79.

indigo-sulphate solution should be added, by which modification the termination of the reaction could be easily and accurately ascertained. Müller found in his experiments that one molecule of ammoniacal sulphate of copper was decolorised by the same quantity of "hyposulphite," as one molecule of indigotin dissolved in sulphuric acid. The standard solution of copper sulphate is prepared by dissolving 1.904 grms. (equivalent to 1 grm. indigotin) of the crystallised salt ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in a litre of water containing 100 cc. of strong ammonia (sp. gr. .880); 50 cc. of this solution are measured into a wide-mouthed flask (capacity 200 cc.), boiled to expel air, and allowed to cool. The flask is provided with an india-rubber stopper perforated with four holes, into two of which are fitted two Mohr's burettes, one containing the hyposulphite solution, and the other the indigo-carmin. The two other apertures serve for the entrance and exit of a current of hydrogen or coal-gas. It is essential that the process should be conducted without access of air. The burette containing the "hyposulphite" is furnished with a perforated cork, through which passes a glass tube connected with a supply of coal-gas; and at the lower extremity a glass tube is joined to it, which is in connection with the bottle filled with sodium hyposulphite above mentioned. By this means the burette can be refilled without fear of oxidising the hyposulphite solution. The flask containing the 50 cc. of copper sulphate is attached to the india-rubber stopper, and the air is expelled by a current of coal-gas, which should first pass through U-tubes containing ferrous hydrate. The solution of hyposulphite is now gradually run in until the liquid becomes nearly colourless, when a few drops of indigo-carmin are added from the other burette, and finally, a further quantity of hyposulphite is added, until the solution assumes a peculiar brownish-red colour. The end of the reaction is sharp and unmistakable. The quantity of hyposulphite which is used to decolorise the few drops of indigo-carmin solution is very small, but by determining the relative strength of the two liquids, the amount thus consumed can be easily calculated, and then deducted from the number of cc. used in the titration of the copper sulphate solution. The 50 cc. of copper sulphate are equivalent to .05 indigotin, so that supposing 25 cc. of sodium hyposulphite have been required for the titration, each cc. of the hyposulphite will correspond to .002 indigotin. Whenever an analysis of indigo is to be made, the hyposulphite solution requires re-standardising.

Titration of the Solution of Indigo.—The operation is performed in a similar manner to that just described. 0.5 grm. of finely-powdered indigo is mixed with ground glass, and dissolved in sulphuric acid as previously stated in detail. The sulphindigotic acid is diluted to 500 cc. and filtered; 50 cc. of the filtrate are measured into a flask, boiled to expel air, and allowed to cool. The flask is then attached to the burettes, and after driving out the air by a current of coal-gas the

hyposulphite solution is gradually added, during constant agitation. With indigotin and the better qualities of indigo the liquid, when fully reduced, becomes of a pale-yellow tint, but with inferior samples the solution is more or less of a dirty brownish-yellow colour. In both cases, however, the end of the reaction is quite clear and distinct.

Action of Sodium Hyposulphite upon the Constituents of Indigo other than Indigotin.—A series of experiments similar to those described under the permanganate method showed that neither indigo-gluten, indigo-brown, nor indigo-red had any appreciable effect upon the estimation of indigotin by sodium hyposulphite. But there is one possible source of error. If the solution to be titrated contains iron in the ferric state, the results obtained are too high. Ferric sulphate, in an acid solution, is reduced quantitatively to ferrous sulphate. The same quantity of hyposulphite solution is required to reduce one molecule of ferric sulphate as to reduce one molecule of sulphate of copper. A standard solution of ferric sulphate in fact may be employed in place of ammoniacal copper sulphate, for determining the strength of the hyposulphite solution. It is only in the lower classes of indigo that iron is present to any appreciable extent, and in those cases it principally exists, or subsequently becomes reduced to, the ferrous state. The hyposulphite method gives the percentage of indigotin, and does not include indigo-red.

Example 3.—50 cc. standard ammoniacal sulphate of copper (= .05 indigotin) required 30 cc. sodium hyposulphite—

$$\therefore 1 \text{ cc. hyposulphite} = \frac{.05}{30} = .0016\bar{6} \text{ indigotin.}$$

1 grm. of Java indigo was dissolved in sulphuric acid, and diluted with water to 1 litre; 50 cc. (= .05 indigo) required 20.6 cc. hyposulphite—

$$\therefore \frac{.0016\bar{6} \times 20.6 \times 100}{.05} = 68.64 \text{ per cent. indigotin.}$$

II. Sublimation.—According to Crum, indigo-blue volatilises in open vessels at about 288° in dark purple-red vapours; in closed vessels it decomposes partially when heated. According to Dumas, it volatilises without decomposition only in a current of air or in vacuo: the powder dropped on a piece of heated platinum foil volatilises in purple vapours, without leaving a residue, each particle being supported by the vapour, without coming in contact with the foil. C. Tennant Lee* has used a method of sublimation for several years, which, in his hands, has yielded most satisfactory results. He employs for this purpose shallow platinum trays, 7 cm. long, 2 cm. wide, and 3 to 4 mm. deep. About .25 grm. of finely-powdered indigo, which has been previously dried at 100°, is weighed into the tray and spread in an even layer over its surface. The operation is conducted on an iron plate, which is heated gradually to avoid

* *Chemical News*, vol. 1. (1884). p. 49. An abstract from the *Journal of the American Chemical Society*.

burning. When the surface of the indigo is covered with a shining mass of crystals, a piece of sheet iron, bent into the form of a low flat arch, is placed over the platinum tray, and, at the same time, as the temperature rapidly rises, the gas is turned down. The vapours of indigotin are now given off, and the heat is gradually raised; but care must be taken lest any yellowish vapours appear, which would indicate the evolution of bodies other than indigotin. When all the crystals of indigotin have disappeared from the surface of the residue, the tray, with its contents, is cooled in a desiccator and weighed. The loss in weight is indigotin. Lee states that the time required for a 50 per cent. indigo is 30 to 40 minutes, but soft Java indigo sometimes requires two hours. He also adds that results obtained by this method are constant within .25 per cent., but frequently he has made re-determinations, with variations of only half that error. At first sight, this method appears remarkably simple, combining accuracy with a fair degree of quickness. Indigo, however, contains a variety of substances whose properties have not as yet been thoroughly investigated. But it has been found that indigo-gluten (including other substances soluble in dilute acid), indigo-brown, &c., are all more or less affected by this process of sublimation, and, furthermore, that pure indigotin (prepared either by Fritzsche's method or by crystallisation from aniline) is partially decomposed, and leaves a dark-brown residue, amounting to upwards of 10 per cent., varying in quantity according to the physical condition of the indigotin operated upon, and also according to the length of time required for the operation. As a rule, inferior qualities of indigo, containing much matter soluble in hydrochloric acid, yield results by this process which are too high; whilst, on the other hand, indigos rich in indigotin give results which undoubtedly are too low. When performed under the same arched cover, a given sample of indigo has yielded almost identical results, but when the two analyses have been made under separate covers, a difference of upwards of 2 per cent. in the same sample has been usually obtained. The estimation of indigotin by sublimation necessarily involves a determination of water in the sample. The principle of the process is a good one, and no doubt further research would yield fruitful results.

III. Methods based upon the Reduction of Indigotin in an Alkaline Solution.—Numerous processes have been proposed to estimate indigotin gravimetrically by means of reducing agents. They have all one end in view—viz., the formation of indigo-white by the action of nascent hydrogen and its subsequent re-oxidation to indigotin. The separation of indigotin from the other matters present in indigo by processes of reduction, although a long and tedious operation is generally considered to give accurate and reliable results. Some of the processes, however, are far from trustworthy. A common method consists in treating finely-powdered indigo, out of contact with air,

with a solution of ferrous sulphate and slaked lime. After gently heating the mixture for some hours the precipitated matters are allowed to subside; a measured volume of the clear liquid is decanted into a beaker, acidulated, and oxidised to indigotin. The precipitate is collected on a weighed filter, washed, dried, and weighed. The results obtained by this process are generally too low, as some of the indigotin is thrown down in the reducing flask with the mixed precipitate of iron oxides and lime.

Reduction by Ferrous Sulphate and Sodium Hydrate.—This method, devised by Crace-Calvert, gives reliable results, but, as described on p. 196 of Crace-Calvert's work on *Dyeing and Calico Printing*, it requires a very long time to complete the operation. The following mode of procedure is recommended:—1 grm. of finely-powdered indigo is placed in a flask with 2 grms. of ferrous sulphate, 5 grms. of sodium hydrate, and about a litre of water. The flask is closed by a cork with three perforations, in one of which is fixed a syphon for running off the reduced indigo; the other apertures are used for the entrance and exit of a current of hydrogen or coal-gas. The mixture is kept at a temperature a little below the boiling point for $1\frac{1}{2}$ to 2 hours, when the source of heat is withdrawn, and the insoluble matters allowed to subside; 500 cc. are syphoned off, and the rest of the liquid in the flask accurately measured. The reduced indigo is allowed to oxidise, which may be accelerated by drawing a current of air through the solution. If the liquid be now filtered, it would generally take at least a day to pass through the filter, and, furthermore, the filtrate would contain in solution a certain quantity of indigotin. On the other hand, if an acid be added to the solution, a variable amount of indigo-brown—dissolved by the caustic soda—would be precipitated with the indigotin and indigo-red. But indigo-brown, as well as indigo-red, is soluble in alcohol, and this property may be advantageously utilised. When the measured volume of reduced indigo has become oxidised, an excess of hydrochloric acid is added, and the precipitate allowed to subside; the clear supernatant liquid is then carefully poured on to a weighed filter, and the residue washed two or three times by decantation with hot water. The residue is now boiled with alcohol, and before filtering the liquid is cooled somewhat, in order that any dissolved indigotin may be deposited. The whole is then transferred to the filter, washed with 80 per cent. alcohol, dried at 100° , and weighed. The weight obtained gives the amount of indigotin in the sample, the indirubin present being removed by the alcohol.

Reduction by Sodium Hyposulphite and Lime.—The following process, devised by Rawson, gives accurate results, and the percentage of indigotin and indirubin may be obtained separately.

1 grm. of finely-powdered indigo is ground into a thin paste with water, and introduced into a 40-oz. flask (A, Fig. 114) with 500

to 600 cc. of lime water. The flask is furnished with an india-rubber stopper, which has three perforations, in one of which is inserted a syphon (B) closed by a pinch-cock, and in another is fixed a funnel (C)

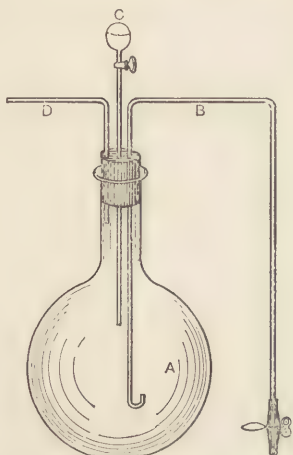


Fig. 114.—Flask for reducing indigo.

provided with a stopcock; the third aperture, by means of a short bent-glass tube (D), serves for the entrance of a current of hydrogen or coal-gas. The flask is connected with the gas supply, and the contents heated to about 80°C . 200 to 250 cc. of a solution of sodium hyposulphite* (NaHSO_3) are now introduced by means of the funnel, and the mixture, which in a few minutes takes a yellow tint, is kept near the boiling point for half an hour. After allowing the insoluble matters in the flask to subside, 500 cc. are syphoned off, and the rest of the liquid accurately measured. The 500 cc. are poured into a conical flask, and by means of an aspirator

a current of air is drawn through the liquid for about 20 minutes. The excess of hyposulphite is thus oxidised to sulphite and the indigo-white to indigotin. Hydrochloric acid is then added to dissolve any carbonate of lime which may have been formed, and the precipitate is collected upon a previously dried and weighed filter, washed thoroughly with hot water, dried at 105°C ., and weighed. The precipitate thus obtained consists of indigotin and indirubin. In order to determine the amount of each of these constituents, the filter with its contents is placed in an extraction apparatus, and the indirubin dissolved by means of alcohol. The alcoholic solution is allowed to cool in order that any indigotin may be deposited, from which it is filtered, evaporated on the water-bath, dried at 105°C ., and lastly weighed. The difference between the first weighing and the second gives the amount of indigotin, from which the percentage may be easily calculated.

Although, with due care, the precipitated indigotin and indirubin may be obtained free from impurities, with certain low classes of indigo, the product is liable to be contaminated with a little brown matter. When indigotin and indirubin are estimated separately, the error falls on the indirubin. The error may be avoided by dissolving the dry alcoholic extract in concentrated sulphuric acid, diluting with water, and carefully and very slowly titrating the filtered solution with $\frac{N}{50}$ permanganate. Or, an aliquot part of the whole precipitate may be dissolved in sulphuric acid, diluted to a given bulk, and a portion

* This solution of hyposulphite should be about four times as strong as that described on p. 803.

titrated with permanganate. In this case, of course, only the combined percentage of indirubin and indigotin is obtained.

Example 4.—1 grm. of indigo was reduced by a mixture of sodium hyposulphite and lime water. The liquid measured 935 cc. 500 cc. were oxidised, and treated as above described. Weight of precipitate = .243 grm.;

$$\therefore \frac{.243 \times 935 \times 100}{500} = 45.44 \text{ per cent. indigotin and indigo-red.}$$

The filter was placed in the extraction apparatus, and the red dissolved by means of alcohol. The alcoholic solution was evaporated to dryness, dried at 100° and weighed. Weight of extract = .0145 grm. From this amount 1 milligramme was subtracted in order to allow for the slight solubility of indigotin in alcohol.

$$\therefore \frac{.0135 \times 100 \times 935}{500} = 2.52 \text{ per cent. indigo-red.}$$

Indigotin (by difference) = 42.92 per cent.

In the *Journal of the American Chemical Society** (1885, p. 16), H. M. Rau describes a modification of Fritzsche's method for the analysis of indigo. From 1½ to 2 grms. of the sample in fine powder are introduced into an 8-oz. Erlenmeyer flask, fitted with a doubly-perforated rubber stopper, through which pass a bent tube provided with a stop-cock, and reaching just below the stopper; and a second tube of syphon shape reaching nearly to the bottom of the flask. This tube terminates in a small funnel, in which a wad of glass wool is placed. From 3 to 4 grms. of pure grape sugar, 15 to 20 cc. of a 40 per cent. solution of caustic soda, 60 cc. of water, and about 120 cc. of 90 per cent. alcohol are added, and the weight of the whole taken; the flask and tubes having been previously weighed alone. A small piece of rubber tubing closed with a pinch-cock is slipped over the syphon-tube, and the flask heated on the water-bath for about half an hour. The reduced indigo readily dissolves, the liquid assuming a deep yellow colour. After about an hour the flask is connected with an apparatus generating carbon dioxide, and the liquid syphoned off as far as possible, the wad of glass wool retaining the solid particles. The flask is again weighed, whereby the weight of the liquid run off is ascertained. A current of carbon dioxide is passed through the liquid for about 15 minutes, and afterwards a current of air, which completes the precipitation. The precipitate is collected upon a previously-tared filter, washed with hot dilute hydrochloric acid, and then with boiling water, dried at 110° C., and weighed.

Rawson finds † that although the amount of indigotin may be accurately determined by this process, the indirubin is not precipitated. This might be overcome, however, by adding a large volume of water before filtering. Among other methods for testing indigo, the following may be mentioned:—

F. A. Owen ‡ reduces the indigo by a mixture of zinc dust and strong ammonia, re-oxidises an aliquot portion of the solution, and weighs the washed and dried precipitate on a tared filter.

* Also *Chem. News*, vol. li. (1885), p. 207.

† *Ibid.*, vol. li., p. 253.

‡ *Journ. of Amer. Chem. Soc.*, Nov., 1888; *Chem. News*, vol. lxxiii., p. 301.

M. Honig* recommends the following process:—From 5 to 8 grm. of indigo is mixed with about 2.5 grms. of finely-powdered dry pumice-stone, and the mixture introduced into a Zulkowsky-Wolfbauer extraction apparatus. About 50 cc. of aniline or nitro-benzene (preferably the former) are used for extracting. The operation is said to be generally completed in an hour, but it is recommended that the mass be removed from the apparatus, washed with alcohol, dried, powdered, and extracted a second time. The solution is afterwards evaporated down to a few cc., and mixed with five times its volume of absolute alcohol. The precipitated indigotin is collected on a weighed filter, washed with alcohol, dried at 110° C., and weighed. There are several objections to this process. Indigotin is by no means readily extracted by aniline; moreover, other substances of a brown colour are somewhat soluble. Indirubin is not determined, since it is removed by the washing with alcohol.

F. Voeller† analyses indigo by estimating the nitrogen which a weighed sample contains after purification. The indigo is placed in a perforated platinum crucible closed with asbestos, and with the aid of a filter-pump washed successively with hydrochloric acid, soda, alcohol, and hot water. The nitrogen in the residue is then estimated by Kjeldahl's method. The nitrogen found multiplied by the factor 9.36 gives the indigotin. An analysis of commercial indigo quoted by Voeller gave 75.76 per cent. of indigotin, 16.35 per cent. of mineral matter, and 6.48 per cent. of water. But commercial indigo containing so much mineral matter and water *never* contains such a high percentage of indigotin. Presuming the method to give accurate results, it would be altogether unsuitable for commercial purposes. Furthermore, the indirubin is removed by washing with alcohol.

Indigo Extract.—The value of indigo extract may be determined by any of the methods given under Section I., *Indigo*, "where the indigo is dissolved by sulphuric acid." The modified permanganate method is the most suitable.‡ About 10 grms. of extract are dissolved in a litre of water; and 50 to 100 cc. of the filtered solution titrated in the presence of sulphuric acid with $\frac{N}{50}$ permanganate, as previously described.

Comparative dye-tests are especially valuable for indicating the purity of shade. Samples of extract of indigo vary very much in this respect. The tests are best made on worsted yarn or cloth; about 5 per cent. of "extract" and 5 per cent. of sulphuric acid are convenient quantities. *Refined* indigo extract should dissolve completely in water, leaving no green or greenish-grey residue. Common indigo extract contains more or less dirty green insoluble substances.

Estimation of Free Acid.—There are "acid" indigo extracts and

* *Zeitschr. f. angew. Chem.*, 1889, No. 10; *Analyst*, 1889, p. 177.

† *Zeitschr. f. angew. Chem.*, 1891, p. 110; *Journ. Soc. Chem. Ind.*, 1891, p. 488.

‡ Except in the case of very impure or adulterated samples, it is unnecessary to precipitate with salt.

"neutral" indigo extracts, but the latter, as sold, frequently also contain more or less free acid. The amount of free acid may be readily determined by precipitating the colouring matter with pure salt. For this purpose 100 cc. of a 1 per cent. solution of the extract is treated with 32 grms. of neutral sodium chloride, and, after standing an hour, with occasional shaking, filtered, and the precipitate washed with a little saturated solution of salt. The filtrate, which is slightly coloured (but this does not interfere with the reaction), is titrated with $\frac{N}{10}$ caustic soda and phenolphthalein. With a little practice, fairly good results may be obtained by titrating direct without resorting to precipitation.

Adulteration.—Samples of indigo extract frequently contain *soluble blue* and similar coal-tar blues. These may be usually detected by dyeing a skein of silk in an acidified solution of the sample, washing, and boiling in a large volume of fresh water. When this is repeated two or three times, almost the whole of the indigo extract is removed, and the aniline-blue remains on the fibre. The presence of soluble blue is also indicated by the action of potassium permanganate on a solution of the sample. With pure indigo extract the solution becomes yellow; whereas, if aniline-blue is present, it changes to a lighter blue, violet, or grey. After destroying the indigo by permanganate, a small piece of wool or silk may be dyed in the solution, and the colour recognised on the fibre by tests given in the tables at the end of this work.

LOGWOOD.

The only reliable method of valuing samples of logwood, or logwood extract, is by means of comparative dye-trials. For this purpose worsted yarn, slubbing, or cloth (in lots of 10 grms. each), is mordanted with 3 per cent. of bichromate of potash and 6 per cent. of tartar. After well washing, each lot of material is dyed in a separate bath with from 5 to 10 per cent. of the logwood samples to be examined. If logwood extracts are being tested, from 2 to 5 per cent. will be found sufficient. The dye-trials are, of course, made simultaneously in the apparatus, which has been previously described. If the samples of logwood be finely rasped, the requisite amount may be carefully weighed out on the balance, and introduced direct into the dye-baths, which must then be boiled for about 10 minutes before placing in the material to be dyed. In the case of chipped logwood, however, since for 10 grms. of wool 10 per cent. only represents 1 gm., it would be almost impossible to obtain a fair average in this way. In order, therefore, to overcome this difficulty, the chipped wood must be reduced to powder, but this cannot be accomplished without previously drying the wood. About 50 to 100 grms. of each sample are dried in a water-bath, and then ground to a fine powder in a small coffee mill. In the meantime the percentage of water is estimated in 10 grms. of each sample, so as to be able to calculate the amount of dried powder equal

to 1 grm. (or 0.5 grm. as required) of the original wood. If, for example, a sample is found to contain 40 per cent. of water, 100 parts correspond to 60 parts of dry wood. Consequently 0.6 grm. of the dried powder would be equal to 1 grm. of the original sample, the amount required for 10 per cent.

Unless the prepared sample be dried immediately before weighing, it will be necessary to estimate the amount of water it has absorbed during the process of grinding and sampling. Perfectly dry logwood, when exposed to the air, quickly absorbs 5 or 6 per cent. of water.

Another method of obtaining an average sample of chipped logwood is to make an alcoholic solution of the colouring matter. From 10 to 20 grms. of the sample are introduced into a large flask fitted with a cork and long glass tube (or the flask may be attached to an inverted condenser), 500 or 600 cc. of alcohol (redistilled methylated spirit answers the purpose) are added, and boiled for about a quarter of an hour. The alcoholic solution is poured off into a litre flask, and the residue boiled up again with 300 or 400 cc. of fresh alcohol. The solution, when cold, is finally made up to 1 litre. If 20 grms. of logwood were weighed out, 50 cc. of the alcoholic solution correspond to 1 grm.

In some cases it is desirable to ascertain the condition in which the colouring matter principally exists in a sample of logwood. Two series of dye-tests should be made; in one case upon wool mordanted chiefly with chromic acid (say 3 per cent. of potassium bichromate and 1 per cent. of sulphuric acid), and in the other upon wool mordanted with chromium oxide (see p. 352). It will frequently be found that under these conditions two samples of logwood give very different results. A sample of freshly cut wood where the colouring matter exists principally as hæmatoxylin will give superior results on "yellow" mordanted wool, whereas matured logwood containing principally hæmatein will give better results on "green" mordanted wool.

In the case of extracts of logwood, it is advisable to weigh out 10 grms. and dilute with water to 1 litre. The requisite amount for the dye-trials may then be measured. Every 10 cc. of such a solution corresponds to 1 per cent. when 10 grms. of material are to be dyed.

Several colorimetric processes have been proposed for valuing logwood and its extracts, but they are not nearly so reliable as carefully conducted dye-trials. Perhaps the best method consists in comparing dilute alcoholic solutions of the colouring matter developed by a solution of alum.

Rawson has obtained fairly good results by working in the following manner:—10 grms. of the sample of logwood (or an equivalent amount of extract) are extracted by alcohol, and made up to 1 litre; 10 cc. of this solution are further diluted with alcohol to 100 cc. Then 5 cc. of the dilute solution are put into a Nessler glass (or colorimeter tube), to which are added 5 cc. of a 1 per cent. solution of alum, and the tube filled to the mark with distilled water. The colour produced (which

develops gradually) is compared with a standard sample treated in exactly the same manner. The value of the sample is, of course, in the inverse ratio of the number of cubic centimetres required to produce the same depth of tint. If the wood be finely ground, 1 grm. may be taken and made up to 1 litre without further dilution.

H. Trimble,* of Philadelphia, recommends the following process for testing logwood extracts:—A solution of a standard extract is made of such a strength that 1 cc. shall contain 0.001 grm. of the dry extract. It is, therefore, first necessary to dry a portion of the sample at 110° C., in order to make the calculation for this solution. Then 1 cc. of the solution is mixed in a test-tube with 1 cc. of a solution of copper sulphate (containing .002 grm. Cu SO_4 , 5 H_2O per cc.) and 10 cc. of water, containing in solution a little calcium carbonate. The mixture is quickly heated to the boiling point, poured immediately into a 100 cc. cylinder, and diluted with distilled water to the mark. The sample of extract to be tested is subjected to the same treatment, and diluted with distilled water until the depth of colour is exactly the same as in the standard, when, on reading off the height of liquid, the comparative value will be known. It is necessary to renew the standard every 10 to 15 minutes, as it fades in that time. Although not stated in the communication, it is obvious, from the description, that the observation is made in the transverse direction of the cylinders, and not through the *depth* of the liquid, which is the usual plan.

During the process of ageing of logwood the ground wood is sometimes sprinkled with an alkali, such as lime water, stale urine, or dilute solution of carbonate of soda. This addition, which must be pronounced fraudulent, gives a temporary bloom to the wood, and causes it to give up its colouring matter to water much more readily. But the colour is much less permanent in the presence of an alkali. If an alkali be present in logwood, the colouring matter will dissolve in distilled water with a violet colour instead of yellowish-orange. The presence of an alkali may also be detected by allowing a little of the wood to steep in distilled water, and adding to the solution a few drops of phenolphthalein. The colour of the logwood solution itself, however, is a sufficient indicator.

The value of chipped and rasped logwood of the same quality varies to a very considerable extent according to the percentage of water which is present. This may be said to range from 32 to 50 per cent. From 38 to 40 per cent. may be taken as a fair average. If the water exceed 42 per cent., the logwood, as a rule, may be moulded into compact balls. In order to determine the amount of water, 10 grms. are dried in the water-oven, or preferably at 105° C. in an air-bath, until they cease to lose weight. From 2 to 3 hours are required to complete the operation. If necessary, after drying, the ash may be determined by ignition at a low red heat. It should not amount to more than 2 per cent.

* *Journ. Soc. Dyers and Col.*, 1885, p. 92.

If it be required to estimate the amount of extractive matter, 5 grms. are placed in a Soxhlet's tube, and the colouring matter, &c., extracted by means of alcohol. When the liquid which syphons off is colourless, or nearly so, the alcohol is distilled, and the residue dried at 105° C. until the weight is constant.

Logwood liquor is not unfrequently found to contain common salt, added in order to raise the specific gravity. It may be easily detected by boiling with a little pure nitric acid (to destroy the colouring matter), and then adding a solution of nitrate of silver, which, in the presence of chlorides, gives a white curdy precipitate.

Logwood extract is sometimes adulterated with chestnut extract. When this is suspected the percentage of tannic acid may be with advantage determined by one of the processes given under *Tannins* (p. 786).

Methods for detecting and estimating various impurities in logwood extract are given by L. Bruehl in the *Journal of the Soc. of Dyers and Colourists*, 1889, pp. 111, 122.

FUSTIC, QUERCITRON BARK, &c.

Comparative dye-tests are made either upon cotton or wool. In the latter case the material is mordanted with 3 per cent. of bichromate of potash, well washed, and dyed in fresh baths with from 20 to 30 per cent. of the yellow woods. In testing extracts 3 to 5 per cent. are convenient quantities. 10 grms. of the extract are made up with water to a litre, and an aliquot part taken for each test. The bottle or flask containing the diluted extract must be well shaken immediately before measuring the required amount. Dye-tests should also be made upon material mordanted with 4 per cent. of stannous chloride and 4 per cent. of tartar. Extracts of fustic, quercitron bark, &c., according to the mode of preparation, vary considerably in shade. Some varieties produce upon "chromed" wool greenish-yellows, while others give brown or orange-yellows. The green shade is generally considered the more valuable, and in making dye-tests this must be taken into consideration. A "red" shade may appear to be deeper and fuller than a "green" shade, when in reality it may contain much less colouring matter. The dyed swatches, after being dried, must be compared by looking "overhand" in various positions when the *depth* of yellow can be much more accurately discerned. In any case, however, yellow shades, especially if not of exactly the same tone, are difficult to accurately estimate by the eye, and it is far better to combine the yellow with some blue colouring matter so as to produce a green. With samples of fustic, &c., good results are obtained by adding 2 per cent. of logwood extract to each bath. A better method, however, is to make the tests upon material which has been previously dyed a light uniform shade of blue in the indigo-vat. In

this way a very small difference in the "yellow" samples is perceived. If a *green* shade of fustic is being compared with a very *red* shade, a small quantity of red colouring matter (such as alizarin-red) should be added to the bath containing the former, and the amount taken into consideration in calculating the value of the samples.

Fustic Extract is liable to contain dextrin, molasses, zinc sulphate, glycerin, alum, turmeric, aniline-yellows, &c. Methods for detecting these bodies are given by L. Bruehl in the *Journal of the Society of Dyers and Colourists*, 1889, p. 124.

TURMERIC.

Comparative dye-tests made either upon wool or cotton give the best results. About 10 per cent. of each sample is taken and dyed with 5 per cent. of alum in a single bath. The value of samples of turmeric may also be obtained by a colorimetric method applied in the following manner:—5 gm. is boiled with about 200 cc. of alcohol for a quarter of an hour, and when cold made up to 250 cc. 5 cc. of the filtered solution are run into a Nessler tube, and made up to 100 cc. with water containing a small quantity of caustic soda.

Powdered turmeric is sometimes adulterated with mineral matter, especially common salt. This may be readily detected by boiling with nitric acid and adding silver nitrate to the solution. The amount is determined by igniting 1 gm. in a platinum crucible, dissolving the ash in water, and titrating the solution with decinormal silver nitrate (p. 738). Good turmeric does not leave more than 5 per cent. of mineral matter.

THE RED WOODS.

Peach Wood, Brazil Wood, Sapan Wood, &c., and their extracts, may be examined in the same manner as logwood. Comparative dye-tests are made by mordanting wool with 3 per cent. of potassium bichromate, and dyeing in fresh baths with about 20 per cent. of the ground woods, or from 2 to 5 per cent. of extracts. Good results are also obtained by mordanting with 8 per cent. of alum and 8 per cent. of tartar. The dye-tests may also conveniently be made upon calico mordanted in stripes with alumina, iron, and chromium respectively. The commercial extracts, which usually have a density of from 5° to 20° Tw., are liable to contain common salt, which, however, may readily be detected by boiling with nitric acid and adding silver nitrate. The rasped woods should not contain more than about 30 per cent. of water.

Camwood, Barwood, and Saunders-wood are best examined in the following manner:—Wool is mordanted with 2 per cent. of bichromate of potash, and then boiled with 10 to 20 per cent. of the dyewood for an hour. It is squeezed (not washed) and worked in the

mordant bath again for about half an hour. Before entering the wool into the dye-bath, the wool should be boiled for 15 minutes. A second lot of yarn or cloth should be dyed in the bath without any further addition, since one sample may give up its colouring matter much more slowly than another.

M A D D E R.

For determining the comparative value of samples of madder and madder preparations, dye-trials are made either upon wool or cotton. Since madder is now almost exclusively used in wool dyeing, dye-tests on wool are of the greater importance. The tests should be made upon cloth, mordanted in one case with 3 per cent. of bichromate of potash, and in a second case mordanted with 8 per cent. of alum and 8 per cent. of tartar. The dyeing should be performed in fresh baths, using 30 per cent. of madder, or an equivalent amount of extract, the value of the samples being in the inverse ratio of the amount of material necessary to produce the same depth of shade.

When madder was used in Turkey-red dyeing, the following process was usually carried out:—Equal weights (5 or 10 grms.) of cotton, mordanted in stripes, with alumina and iron mordants, were placed in separate dye-vessels, heated by one large copper bath in the manner already described (p. 789). Equal weights (about 5 grms.) of the samples of madder were added to the various dye-pots, and the temperature gradually raised to 75° C. during the course of 1½ hours, and then heated for 1½ hours further at or near the boiling point. The pieces were then taken out, washed, and compared, and a second series of tests made with quantities of madder judged sufficient to produce the same depth of shade in each case. The total colouring power of the samples was thus obtained, but a further operation was deemed necessary. The dyed swatches were cut into two parts, and one of each was submitted to a treatment in weak soap solution for half an hour, at a temperature of 70° C. The swatches were then washed, dried, and compared with each other, and with the swatches which had not been soaped.

The method of testing alizarin at the present day is practically the same; much smaller quantities of colouring matter being, of course, taken.

Madder has been found adulterated with a great many substances, both of organic and inorganic origin. Of mineral matters, powdered brick, yellow ochre, sand, and clay have been found; while the organic impurities comprise such bodies as sawdust and ground red and yellow woods.

An adulteration with mineral substances is usually easily ascertained by incinerating a weighed amount in a platinum crucible. Good madder should not leave more than 5 to 10 per cent of ash, whereas adulterated samples may leave very much more. Some of the mineral substances

used for adulteration may also be detected by shaking up the madder with water, and, after allowing the mixture to stand for a short time, pouring off the turbid liquid. The madder remains suspended in the water, whereas the mineral substances quickly subside. By repeating the operation two or three times, the impurities may be obtained free from madder, and can then, if necessary, be further examined.

Persoz devised a very simple method for ascertaining the presence of ground dyewoods, &c., in madder. A piece of filter paper is immersed in a weak solution of stannic chloride, and a similar piece in a solution of ferric sulphate. The test papers are then separately placed on glass plates, and a little of the madder sprinkled over them. After a short time (a quarter of an hour or so) the papers are examined. The possible adulterations of madder produce the following effects:—

Stannic Chloride Paper.

Brazil wood, peach wood, &c.,	. . .	crimson-red.
Logwood,	purple.
Fustic, quercitron, &c.,	. . .	deep yellow.
Madder,	very faint yellow.

Ferric Sulphate Paper.

Logwood,	violet-black.
Tannin matters,	deep greenish-black.
Madder,	very light brown.

Schlumberger estimates the amount of pure colouring matter in madder as follows:—10 grms. of madder are treated with 500 cc. of water acidulated with acetic acid at 30° C. for 24 hours, and then filtered and washed. The residue is boiled 10 minutes with a litre of dilute acetic acid (sp. gr. 1.005) and filtered. The residue is again boiled with a fresh quantity of the same acid and filtered. The solutions on cooling deposit the colouring matter in orange-coloured flakes; some, however, remains in solution, and is precipitated by adding common salt. The precipitate is collected on a small tared filter, washed, dried, and weighed. Schlumberger found by this method from 4 to 4.2 per cent. of colouring matter in good Avignon and Alsace madders. Inferior qualities gave from 1.9 to 2.7 per cent. only.

CUDBEAR AND ORCHIL.

The colouring principles in these bodies being practically the same, they may be examined by the same processes. In order to determine the value of a number of samples, comparative dye-trials on worsted yarn or cloth are made. In the case of cudbear about 3 per cent. will be found a convenient quantity, and about 5 per cent. of orchil. Dye-tests should be made both in neutral and in acid solutions. It is also advisable to dye in the first case neutral, and afterwards add acid (3 per cent. of sulphuric acid) and dye a second lot of material in

the same baths. In this manner certain adulterations are easily and readily detected. When *cudbear* is to be examined, the requisite amount is carefully weighed out on the balance and added to the dye-bath, which is kept in ebullition about a quarter of an hour before the material to be dyed is introduced. In the case of *orchil liquor* it is not advisable to weigh out direct, since it would be difficult to obtain a fair average portion in the small amount required for 10 grms. of material. Weigh out 10 grms. of the sample (being careful to shake the bottle immediately before weighing), dilute to 1000 cc., and, after well shaking, measure quickly the quantity required in a graduated cylinder. When the temperature of the baths is the same, the yarn or cloth, previously wetted out, is introduced, and dyed for one hour. Whenever samples of orchil liquor are taken from casks, it is most important that the liquid should be thoroughly agitated by means of rakes. Mistakes have often been known to arise from a want of care in sampling orchil liquor.

Cudbear and orchil, being somewhat high in price, are frequently adulterated with some of the coal-tar colours, more especially magenta, and occasionally with some of the red woods. Sometimes both classes of dyes are present. During the past few years many new azo-dyes have been introduced into the market, which yield shades very similar to that of orcein.

Several methods of detecting these various adulterations have been proposed, but many of them are only of any use when the foreign colouring matter is present in comparatively large quantities.

F. Breinl* has recently studied the reactions of a number of coal-tar colours, similar in shade to orchil. He divides them into three groups—(1) The sulphonic acid derivatives of magenta, &c. (2) Magenta, and basic colouring matters from magenta-residue and safranine. (3) The azo-dyes. The reagents employed for detecting the various adulterations are a mixture of hydrochloric acid and stannous chloride, basic lead acetate, common salt, caustic soda, concentrated sulphuric acid, concentrated nitric acid, and concentrated hydrochloric acid.

The most suitable method of proceeding in examining orchil and cudbear is to test them in succession with respect to the single groups. From 1 to 2 grms. of the sample are boiled with 100 cc. of water and the solution filtered; 15 to 20 cc. of the tin solution (made by dissolving 10 grms. of stannous chloride in 25 cc. of concentrated hydrochloric acid and 50 cc. of water) are added, and again heated to boiling. If, after some minutes of continuous boiling, the liquid appears only yellow or yellowish-brown, no colouring matter of group I. is present; but if the liquid retains a red or reddish-violet colour, acid magenta, red-violet, or an acid colouring from magenta-residues is present. With respect to group II. the orchil or cudbear is dissolved

* *Mitth. d. Techn. Gewerbemuseums in Wien*, 1887, p. 37; *Journ. Soc. Dyers and Col.*, 1888, p. 46.

in absolute alcohol (about 20 cc. for 1 grm. of material), and water added until the solution contains about 25 per cent. of alcohol. Basic acetate of lead at 52° Tw. is then added to the solution, in the proportion of about 10 cc. for every gramme of extract. In this manner the natural colouring matter is precipitated, whilst magenta, safranine, &c., remain in solution. If the filtrate is quite or nearly colourless, none of these basic coal-tar colours is present; but if it has a distinct crimson colour and a yellow fluorescence, the sample contains *safranine*, the presence of which may be confirmed by the sulphuric acid reaction. If, however, the alcoholic filtrate is of a red colour without fluorescence, it is tested, after removal of the alcohol, with nitric acid. If this produces only a yellowish-brown colour without fluorescence, pure *magenta* is present; but if a yellowish-green fluorescence is perceived, it indicates the presence of a basic colouring matter from magenta-residues (*cerise*, *grenadine*, &c.).

In order to test for colouring matters of group III. (azo-dyes), a fresh portion of the sample is boiled with water (about 100 cc. for 1 grm. of substance), left to cool, filtered, and the filtrate saturated with common salt. Most of the coal-tar colours of this group are completely precipitated, but at the same time a little of the orcein is also thrown down. If a precipitate be obtained, it is thrown on a filter and washed with a saturated solution of common salt containing a few drops of dilute caustic soda until the filtrate runs off quite or nearly colourless. If there is still a residue, it is dissolved in hot water and the solution treated, after cooling, with concentrated sulphuric acid. The sulphuric acid is added, so that it may collect at the bottom of the test-tube. If a violet, green, or blue zone is obtained, the presence of a colouring matter of group III. may be stated with certainty; the other reactions, as well as dyeing experiments on wool or silk, will furnish further information as to its nature. If, however, sulphuric acid produces a red or brown zone, this only indicates orcein, which was precipitated by salt and not completely washed out.

A. Kertész* tests for *acid magenta* in orchil and cudbear as follows:—A small quantity of the sample is boiled up with water and filtered. The filtrate is mixed in a test-tube with benzaldehyde; equal parts of stannous chloride and hydrochloric acid are added, and the whole well agitated and allowed to settle. If no acid magenta be present, the lower layer of liquid will appear colourless, while in the presence of that colouring matter it becomes of a magenta colour. The solution should be very dilute for this test.

H. Crossley† describes a quick and simple method for detecting the presence of *magenta* in orchil and cudbear. A small portion of the dry substance, in powder, is placed upon a piece of white blotting or filter paper. Two or three drops of aniline-oil or benzal-

* *Journ. Soc. Dyers and Col.*, 1885, p. 217, from *Dingl. Polyt. Journ.*

† *Journ. Soc. Dyers and Col.*, 1886, p. 23.

dehyde (preferably the former) are then poured over it, and if any magenta be present, it is at once dissolved, and colours the paper to a greater or lesser extent, according to the quantity of the adulterant contained in the sample. It should be observed that *pure* orchil and cudbear give *gradually* a pale pink tint, but in the case of magenta the paper is *immediately* coloured. In making use of this test, it should be applied at the same time to a sample of cudbear of undoubted purity. The test is fairly reliable, except when the magenta is present in very minute quantities. In order to approximately estimate the amount of magenta in cudbear or orchil, Crossley makes a solution of the sample, filters, and evaporates to dryness. The dry residue is then digested with strong ammonia, filtered, and washed with ammonia until the filtrate is colourless. The magenta base remains on the filter, which may be dissolved in alcohol, evaporated to dryness, and weighed. Since, however, rosaniline is appreciably soluble in alkalies, the method can only be applied with anything like accuracy to samples containing comparatively large quantities of magenta. A very small amount would probably be entirely overlooked.

Liebmann and Studer * propose the following process for the detection of magenta and acid magenta in cudbear and orchil:—1 grm. of the dyestuff is boiled with 100 cc. of water, and, after cooling, saturated with sulphurous anhydride. Most of the cudbear is thus precipitated. The magenta or sulphonated magenta remains, however, entirely in solution—not as such, but in combination with sulphurous acid. If now acetone be added to this solution, and magenta or acid magenta is present, the colour turns after a few minutes' standing into a violet, while genuine cudbear does not show any change of colour.

In the dyehouse laboratory, it is a common practice to test for magenta in orchil and cudbear, by dyeing a piece of mordanted cotton in a solution of the suspected sample. On the ground that cotton has no affinity for the natural colouring matter, the production of a reddish tint is taken to indicate the presence of magenta in the sample. This process has several weak points. In the first place, an average sample of orchil or cudbear will produce *per se* a deeper tint on mordanted cotton than a certain small amount of magenta which may be present in such a small quantity of orchil or cudbear. Again, if the sample contain a red wood—*e.g.*, barwood or Brazil wood—such a test would be of little use for detecting magenta. There is another important point bearing upon this matter which is not generally known—*viz.*, that the process of manufacture can be so modified that the resulting orchil or cudbear will dye mordanted cotton to a considerable extent. Such being the case, a dye-test without further proof would leave considerable doubt regarding the absence or presence of magenta in a suspected sample.

* *Journ. Soc. Chem. Ind.*, 1888, p. 287.

The detection and estimation of minute quantities of magenta in orchil and cudbear has been studied by Rawson.* The method is based upon the *complete* precipitation of orcein in an aqueous and alcoholic solution by basic acetate of lead, followed by an excess of ammonia. Magenta-base, under the same conditions, remains in solution. It will be observed that the principle is similar to that of Breinl's process, which has been already described; but it had been previously noted that, although basic acetate of lead threw down most of the cudbear, a considerable amount still remained in solution, and it was only after adding an excess of ammonia, or soda, that the natural colouring matter was *completely* precipitated. The process is carried out in the following manner:—

From 1 to 2 grms. of cudbear (or an equivalent amount of orchil liquor) are boiled with 50 cc. of alcohol, and afterwards diluted with 100 cc. of water; 15 to 20 cc. of a strong solution of basic acetate of lead (sp. gr. 1.25) are then added, followed, after stirring, by a similar quantity of strong ammonia. The mixture is filtered, and if the amount of magenta present is to be *estimated*, the precipitate is washed with a solution containing 1 part of ammonia, 5 parts of alcohol, and 10 parts of water; otherwise the washing may be neglected. With pure cudbear the filtrate is quite colourless; if magenta be present it is either colourless or pink, according to the amount of ammonia present in the solution. The liquid is then acidulated with acetic acid, when the presence or absence of magenta is at once made apparent; in the case of pure cudbear or orchil the solution remains colourless, whereas, if a salt of rosaniline be present, the well-known colour of magenta is immediately developed. If further proof be wanting, a small piece of worsted yarn may be dyed in the solution and afterwards tested in the usual way with such reagents as hydrochloric acid, caustic soda, and a mixture of hydrochloric acid and stannous chloride.

By means of this method 1 part of magenta in 100,000 parts of cudbear can be detected.

For determining the *amount* of magenta present a colorimetric process is used. A standard solution of pure magenta is prepared so as to contain $\frac{1}{100}$ milligram. per cc. It is acidulated with acetic acid in order that it may be under the same conditions as the solution to be tested. The latter is made up to a known bulk, say 250 cc. (or, if the quantity of magenta present be very small, concentrated to 100 cc., and the whole taken for estimation), and an aliquot part run into a Nessler tube, and diluted to 100 cc. The standard solution of magenta is then run from a burette into a second cylinder in such quantity that the depth of colour is equal to that in the first, as in the case of Nesslerising ammonia. The amount of magenta present in the sample of cudbear or orchil under examination can be then readily calculated. In place

* *Journ. Soc. Dyers and Col.*, 1888, p. 68; *Chemical News*, vol. lvii. (1888), p. 165.

of Nessler tubes the colorimeter or Lovibond's tintometer (pp. 794 and 796) might be used with advantage.

It will no doubt be apparent from what has been already stated that this method is capable of detecting very much smaller quantities of magenta than the manufacturer of cudbear would ever think of using for the purpose of adulteration. But as the amount present can at the same time be easily and readily estimated, there is little danger of a sample of genuine cudbear which may have become accidentally contaminated with a trace of magenta being pronounced sophisticated.

The method is also applicable to the detection of methyl-violet and safranine. The base of the latter is much more soluble in ammonia than the bases of methyl-violet and magenta. The three colouring matters may be easily distinguished from one another. On the addition of acetic acid to the ammoniacal filtrate, the solution becomes of a bluish-violet tint if methyl-violet be present. Under the same conditions solutions of safranine and magenta are pink or bluish-red. Strong ammonia decolorises methyl-violet and magenta, whereas it produces little or no effect upon a solution of safranine. Strong hydrochloric acid added to a solution of safranine changes the colour to blue; solutions of magenta and methyl-violet with the same reagent become of a pale yellow colour. In place of, or in addition to, these tests, a small piece of worsted yarn may be dyed in the neutralised solution (after the removal of the cudbear, as already mentioned), and the colouring matter identified in the usual way on the dyed material.

Azo- or oxyazo-red dyes (pp. 518-530), when present in cudbear, may usually be readily detected by the formation of a green, blue, or violet-coloured streak when a little of the sample is thrown on the surface of concentrated sulphuric acid. In some cases, however, the colour would scarcely be distinguishable from that given by genuine cudbear, when it would be necessary to make further experiments. For the detection of this class of colouring matters the following mode of procedure gives very satisfactory results:—From 5 to 10 grms. of worsted yarn are dyed (for about an hour) with about 10 per cent. of cudbear either in a neutral bath, or with the addition of a few drops of ammonia. A fresh quantity of yarn is then dyed in the same liquor in exactly the same manner. In this way the greater portion of the cudbear is removed from solution. A small quantity of sulphuric acid (3 per cent. on the weight of the yarn) is now added, and a third lot of worsted yarn dyed in the liquor. The azo-red, under the altered conditions of the bath, works on to the fibre (with a little cudbear), and may be afterwards identified by certain well-known means. At the same time it is advisable, although not absolutely necessary, to treat a sample of cudbear known to be genuine in exactly the same manner.

Ground red woods, such as sanders-wood and barwood, are sometimes added to cudbear, and extracts of the red woods to orchil liquor.

These substances are best detected by means of dye-tests upon cotton, mordanted with salts of alumina. Since the colouring matter of barwood, &c., is not easily extracted by water, it is preferable to make these tests in the following manner:—About 2 grms. of the suspected sample of cudbear are boiled 10 minutes with 50 cc. of alcohol, and then diluted to 200 cc. with water. A strip of mordanted cotton is boiled in this solution for half an hour, and allowed to remain in the bath about half an hour longer, when it is taken out and well washed. With *genuine* cudbear the mordanted cotton assumes a faint pink colour, which also remains after washing. This colour, however, may be almost completely removed by boiling the cotton for a few minutes in alcohol, which treatment does not appreciably affect the colour produced by barwood, &c. If, after boiling with alcohol, the cotton is of a decidedly red colour, it may be safely assumed that the sample of cudbear under examination contains one of the red woods. This may be confirmed by moistening the dyed cotton with a mixture of stannous chloride and hydrochloric acid.

The method of testing orchil and cudbear for red woods, as frequently given, by boiling with a solution of stannous chloride, cannot be recommended.

Samples of cudbear often contain considerable quantities of common salt. This may have been added by the manufacturer merely to reduce the strength of the cudbear to a given standard, or it may have been added as an adulteration. As much as 80 per cent. of common salt has been found in a sample of cudbear. Good genuine cudbear, on incineration, leaves on an average about 6 per cent. of mineral matter, which contains about 1 per cent. of chlorine, as chlorides. For the estimation of mineral matter and chlorides, about 1 gm. of the sample is heated to low redness in a platinum crucible until the residue is of a uniform grey colour. The ash should not be allowed to fuse. If the mineral matter be not more than 7 or 8 per cent., it is quite unnecessary to determine the amount of chlorides. If considerable, the ash is treated with water, and diluted to a known volume, say 500 cc., and filtered. An aliquot part of the filtrate is then placed in a porcelain basin, a drop or two of potassium chromate added, and titrated with a decinormal solution of silver nitrate.

If orchil liquor be found to contain common salt, it can only be regarded as having been fraudulently added with the intention of raising the specific gravity.

COCHINEAL.

Genuine samples of cochineal vary very considerably in colouring power. On account of the comparative high price of the dye, it is frequently adulterated, though not at the present day to such an extent as it was formerly. In some cases the colouring matter is merely partially extracted by a short immersion in water. After re-drying, the

material is sold as black cochineal, or it is shaken up in a sack with talc, barium sulphate, or lead sulphate, and sold as white or silver cochineal.

The value of cochineal samples is best ascertained by making comparative dye-tests. For this purpose several lots of 10 grms. of wool (yarn or cloth) are mordanted with 4 per cent. of stannous chloride and 4 per cent. of tartar. The material should be entered at about 50° C., and the bath gradually raised to the boiling point. After washing, the mordanted wool is dyed in fresh baths, with about 5 per cent. of each sample (ground) for 1 hour. The tests may also be made in a single bath (as in cochineal-scarlet dyeing), using in each case 3 per cent. of stannous chloride, 3 per cent. of oxalic acid, and 10 per cent. of cochineal. On comparing the dried swatches, a decision must be made as quickly as possible, otherwise the eye becomes soon fatigued, and is unable to appreciate a small difference in depth of shade. When a number of samples have to be examined the eye should be allowed to rest now and again on cloth dyed a bright green.

Samples of cochineal may also be conveniently estimated by a colorimetric method in the following manner:—25 grm. of each sample, finely powdered, is boiled with about 200 cc. of alcohol for a quarter of an hour, and, on cooling, made up to 250 cc. with alcohol. 5 cc. of the filtered solution, with 1 cc. of a 1 per cent. solution of alum, are introduced into a Nessler tube and diluted with water to 100 cc. The colour develops gradually in the course of 2 or 3 minutes. The samples are compared with a standard, the value being in the inverse ratio of the number of cc. required to produce the same depth of tint.

Various volumetric processes depending upon the oxidation of the colouring matter have been proposed, but none gives such good and reliable results as either the colorimetric or the dye-trial method. Penny's process, which depends upon the action of potassium ferricyanide, is carried out as follows:—1 grm. of finely-powdered cochineal is treated with a dilute solution of caustic soda, whereby the colouring matter is dissolved. A solution of potassium ferricyanide, containing 5 grms. of that salt per litre, is then gradually added from a burette until the purple colour changes to a reddish-brown.

Such adulterations as barium sulphate, lead sulphate, &c., may be detected by immersing the cochineal in warm water, when the mineral matters settle to the bottom. The cochineal may also be ignited in a crucible, and the ash examined for adulterations. Genuine cochineal leaves less than 1 per cent. of ash. An approximate idea of the value of samples of cochineal is obtained by taking the specific gravity. Adulterated samples are much heavier than genuine cochineal.

CUTCH AND GAMBIE.

The only reliable method for dyeing purposes is to make comparative dye-tests. The estimation of the amount of catechu-tannic acid present

is of no value whatever. Cotton or worsted yarn, in lots of 10 grms. each, is dyed at a boiling temperature with 10 per cent. of cutch and 1 per cent. of copper sulphate for 1 hour. For wool about a litre of water is used, but for cotton not more than 500 cc. The dye-liquor is not exhausted, hence it is very important to have exactly the same volume of liquid in each case. The material is allowed to gradually cool in the liquid for a period of 3 hours, when it is taken out, squeezed, and worked in fresh hot baths for half an hour with 2 per cent. of bichromate of potash. The hanks are then washed, dried, and compared.

Samples of cutch and gambier vary greatly, not only as regards their tinctorial power, but also in respect to the shades which they yield when dyed under identical conditions. Some samples give very red browns, others yellow- or olive-browns. Cutch and gambier are frequently adulterated with mineral substances, clay, &c., and occasionally with starch. Excess of mineral matter is readily determined by igniting a weighed amount in a crucible. Good cutch should not leave more than about 3 per cent. of mineral matter. The percentage of water usually varies from 15 to 25, with an average of about 20.

THE COAL-TAR COLOURS.

With few exceptions, the coal-tar colours as a class (like the natural colouring matters) can only be satisfactorily valued by means of experimental dye-trials. The exact mode of procedure varies according to the properties of the colouring matter, and to the purposes to which it is to be applied. General methods of making comparative dye-tests are given on pp. 789-793; and in Part VII., the mode of application of all coal-tar dyes will be found. In conducting these dye-trials a given weight of colouring matter (about 1 grm.), whenever possible, should be dissolved in a litre of water, and an aliquot part taken. With pure colouring matters not more than from .2 to .5 per cent. should be taken. In the case of paste dyes, such as the alizarins, from 2 to 5 per cent. will be required. As previously stated under comparative dye-tests, the results are only of value when the conditions in each case are identical, or as nearly so as possible. When comparatively small quantities of colouring matters are used, wool and silk in the majority of cases leave but little colour in the bath. In some cases, however—with alkali-blue, for example—a large proportion of colour is left in the bath. In making comparative tests of such dyes, a second lot of material should always be dyed without any further addition. In many cases colorimetric tests afford much useful information. The observations serve either as a preliminary to making dye-tests, or as a confirmation of them. Colorimetric tests are not of much value unless the dyes under examination are of the same kind, and of a similar shade. Methods of making these tests are given on pp. 793-797, under *Colorimetry*. There are very few published methods for deter-

mining the value of colouring matters other than by experimental dye-tests.

In the *Journal of the Society of Dyers and Colourists* (1888, p. 82) Rawson describes a "method for determining the value of naphthol-yellow and certain other coal-tar colours." The principle of the process might be applied in numerous other cases.

Naphthol-yellow S occurs in the market under various names and of various degrees of strength. Some qualities are practically pure, whilst others contain more or less sulphate or chloride of sodium. The method employed for determining the tinctorial value depends upon naphthol-yellow forming an insoluble precipitate with a solution of night-blue, tetramethyltolyltriamidodiphenylnaphthylcarbinol hydrochloride (p. 481).

A standard solution of *night-blue* is prepared by dissolving 10 grms. in 50 cc. of glacial acetic acid, and diluting with water to a litre. Solutions of the samples of naphthol-yellow S are prepared so as to contain 1 gram. per litre. The operation is carried out as follows:—10 cc. of night-blue solution are carefully measured into a small flask, and then about 30 cc. of the solution of yellow run in from a burette; the mixture is well shaken for about a minute, and then poured on to a filter. If the filtrate be of a distinct yellow colour, a second experiment is performed in a similar manner with a smaller quantity of the solution of yellow; if the filtrate be blue or *even colourless*, more of the yellow solution is required. These experiments are repeated with varying quantities of the naphthol-yellow solution until the filtrate possesses a very faint, scarcely perceptible, yellow tint. It is best to collect the filtrate in clear Nessler glasses. With a little practice, the number of experiments for each sample may be reduced to three or four. The value of the samples under examination will be in inverse proportion to the number of cc. required to precipitate 10 cc. of night-blue. For example, if of two samples, one requires 28 cc. and the other 35 cc., their relative value will be as 35 : 28, or expressed centesimally as 100 : 80. If it be desired to express the percentage of pure colouring matter present in the samples, the night-blue solution may be standardised by means of recrystallised naphthol-yellow S, which is the potassium salt of dinitro- α -naphthol-sulphonic acid. 1 gram. of *commercial* night-blue precipitates about 0.25 gram. of pure dry naphthol-yellow S. It would thus appear that two molecules of night-blue combine with one molecule of naphthol-yellow S to form the insoluble precipitate.

The method is applicable to the valuation of the azo-dyes, but in such cases it must be used with discretion. Colouring matters which are to be compared with one another must possess a similar constitution. It would not be correct, for example, to compare a crocein-scarlet with a xyloidine-scarlet. But a number of samples of either of these scarlets, containing various proportions of either mineral or organic

adulterations, can be valued by the night-blue process with great precision.

P. Kay and J. R. Appleyard,* at the suggestion of Knecht, have applied the process to the valuation of picric acid. In this reaction one molecule of night-blue was found to precipitate one molecule of picric acid. They also found that crystal-violet (hexamethyl-rosaniline hydrochloride) gave a similar insoluble precipitate with picric acid. Kay† further shows that picric acid may be estimated by means of a standard solution of caustic potash, using phenolphthalein as an indicator. Of course the method is only applicable in the absence of acid or alkaline salts.

Some coal-tar colours may be estimated by means of a standard solution of *sodium hyposulphite*‡ in a similar manner to that already described for indigo (p. 803). The operation must be conducted in a closed vessel, from which the air has been expelled by a current of carbon dioxide, and since the decolorisation takes place only at 100° the liquid under examination must be raised to the boiling point. One molecule of dyes, such as magenta, Hofmann's violet, Paris violet, &c., requires for complete decoloration the same quantity of hyposulphite as that which is required to reduce two molecules of ammoniacal copper sulphate.

Whatever means are adopted to determine the *amount* of colouring matter present in commercial dyes, practical dye-tests will always be required to ascertain the shades which they are capable of producing on the textile fibres.

Impurities.—Some of the commercial artificial dyes consist of practically pure colouring matters, many others contain more or less impurities of manufacture, and a numerous class contain mineral salts as well as organic substances purposely added. Sodium chloride, sodium sulphate, and dextrin are the most common substances present, but sodium carbonate, magnesium, potassium, and ammonium salts may occasionally be found. The presence of any of these bodies in an artificial dye does not necessarily indicate adulteration, unless, of course, the product is represented as a *pure* colouring matter. In many cases the pure colouring matter cannot be conveniently prepared on a commercial scale, and as the manufactured product is liable to vary in strength, it is reduced to a given standard by some inert substance. Sodium sulphate is used largely for azo-dyes; dextrin and common salt for basic dyes.

Sulphates may usually be detected by adding hydrochloric acid and barium chloride to a dilute solution of the dye. In some cases it is preferable to precipitate the colouring matter by *pure* sodium chloride, and test the filtrate, as above. Alkaline salts of sulphonated dyes leave, on ignition, alkaline sulphates, so that the presence of a sulphate

* *Journ. Soc. Dyers and Col.*, 1888, p. 84.

† *Ibid.*, 1888, p. 84.

‡ *Watts' Dict.*, viii., p. 87.

in the ash does not indicate the presence of sodium sulphate in the colouring matter. In the absence of sulphates, the detection of sulphuric acid in the ash indicates the presence of a sulphonie acid group or groups in the colour.

Chlorides in many cases may be detected by simply adding nitric acid and silver nitrate to a dilute solution of the dye. If the colouring matter is soluble in strong alcohol, it should be extracted by warming with that solvent and the residue tested for common salt.

Dextrin may generally be recognised by its smell when the dye is dissolved in warm water; also by its insolubility in alcohol. When it has been mixed in the dry state (which is usually the case), it is best detected by means of the microscope.

Mixed Dyes.—Many of the dyes found in commerce sold under various names are mixtures of two or more colouring matters. When the dyes have been mixed in the powdered state, they may be recognised in the following manner:—A filter paper is moistened with water or alcohol, and a little of the powdered dye is gently blown on to it. Each particle slowly dissolves, forming a little streak, and if more than one colouring matter is present it is readily detected. Mixtures of many of the azo-dyes are more easily recognised by blowing a little of the powdered substance over the surface of concentrated sulphuric acid contained in a porcelain basin. When the colouring matters have been mixed in solution and evaporated together, the above tests are not reliable. In such cases successive lots of wool, silk, or cotton are dyed in a solution of the sample and the shade compared. The dyed swatches are dried, and small pieces tested with various reagents according to the tables given at the end of this work. If the sample was a mixture, the first swatch dyed will probably show different reactions to the last. Mixtures of dyes may also be detected by means of *capillary analysis*.

The following abstract of a paper by Goppelsröder on this subject is taken from the *Journal of the Society of Dyers and Colourists*, 1888, p. 5:—

Based upon some experimental researches of Schönbein in 1862, which showed that different substances when dissolved in water have a different velocity of propagation by capillary attraction in porous material, such as unsized paper, Goppelsröder has examined in particular the behaviour of colouring matters in this respect. The colouring matters, or mixtures of them, were, if possible, dissolved in water or alcohol, or, if these liquids proved ineffective, in some other solvent which had no chemical action. The porous medium employed was pure (Swedish) white filtering paper, cut into strips of different breadth and length, according to the quality and complexity of the (not concentrated) colour solution under examination. A number of such strips of paper, C, were suspended at one end, B, while 5 to 10 millimetres of the other ends, D, were made to dip into the solution contained

in a series of glasses, as indicated in the annexed diagram (Fig. 115). The time of immersion was usually 15 minutes. By the action of capillary attraction the water contained in the solution begins to rise in the paper, reaching a greater height in a given time than all other substances. Picric acid stands next in velocity of rising, and by dipping a strip of filtering paper into an aqueous solution containing picric acid and turmeric, three

different zones will appear on it after a given time—a highest narrow zone containing water, a middle broad zone of yellow picric acid, and a third and lowest zone of the appearance of the yellow colouring matter of turmeric. By immersing the strip of paper into a dilute solution of potash, the zone of picric acid disappears, while the zone

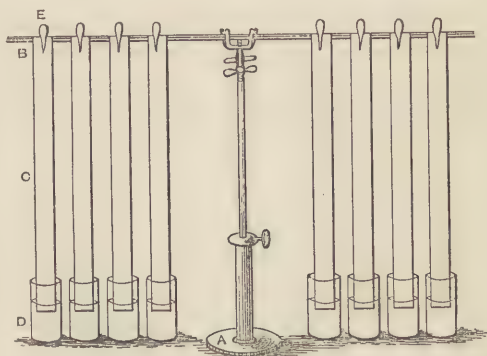


Fig. 115.—Apparatus for capillary analysis.

with the turmeric turns brown; a single operation is, therefore, sufficient for nearly complete separation of the two colouring matters. If now the lowest zone of turmeric yellow is cut off, and the colouring matter contained in it dissolved in alcohol, a repetition of the operation with a fresh strip of paper will again produce three zones—the highest containing alcohol, the middle zone a few lines in breadth, and coloured a very faint yellow with the picric acid. The turmeric zone turns brown in gaseous ammonia, while the zone of picric acid remains unaltered; in a weak alkaline solution the latter is decolorised, the picric acid being dissolved.

By operating upon a mixture of an aqueous solution of picric acid and one of indigo extract, four zones were obtained, when the solution had a purely green colour without prevalence of blue or yellow—a lowest broad zone of a greenish colour, above it a second much narrower zone of pure yellow, above this a third zone containing dilute sulphuric acid, and a fourth zone containing pure water, a drop of tincture of litmus not turning red when applied to it. Three zones only were obtained from a mixture of a little picric acid with much indigo extract—a lowest rather broad zone of an intense bluish-green, a middle purely yellow zone, and a highest zone of sulphuric acid, no water being separated in this case.

In commercial magenta prepared by the reaction of arsenic acid on aniline-oil, traces, at least, of a yellow colouring matter could always be distinctly detected by capillary analysis. But if the filtering paper is dipped a few millimetres into an alcoholic solution of a well crystal-

lised salt of rosaniline, four zones are observed after a few minutes; a highest colourless zone of pure alcohol, and three others of a light pink, pink and deep red in succession. An addition of a trace only of picric acid produces (1) a pink and deep red coloured zone, (2) a colourless zone, (3) a narrow zone of picric yellow. The more picric acid was added to the magenta, the broader was the yellow zone of picric acid, and the narrower the brownish-red zone of magenta. Samples of commercial magenta produced, besides the red zone, a more or less broad yellow zone, which appears most distinct if the alcoholic solutions of magenta are employed in a very concentrated state, and if the filter paper is immersed long enough for the deposition on it of the magenta with a dark brownish-red colour.

Recognition of Artificial Colouring Matters.—Much information may usually be obtained regarding an unknown colouring matter by dyeing cotton, wool, and silk under various conditions. For this purpose a small water-bath, with six apertures to receive little beakers or boiling tubes, may be used with advantage. A solution of the colouring matter is placed in each vessel, and the following tests made :—

- No. 1. Unmordanted wool; solution neutral.
- „ 2. „ „ with addition of a few drops of dilute sulphuric acid.
- „ 3. Wool mordanted with bichromate of potash; solution neutral.
- „ 4. Unmordanted cotton; solution neutral.
- „ 5. „ „ with addition of a little sodium carbonate.
- „ 6. Cotton mordanted with tannic acid and tartar emetic; solution neutral.

The above tests may, of course, be varied or supplemented as desired. After boiling for about a quarter of an hour, the small swatches are taken out and washed, when the results will broadly indicate the class of colouring matter to which the dye belongs. The dyed material may then be dried and tested with various reagents, and the results compared with the tables (pp. 840-873).

A more systematic method of examining artificial colouring matters is given in the *Journal of Society of Dyers and Colourists* (1887, p. 66) by Weingaertner.

The colouring matters are in the first place classified according to their solubility or insolubility in water, and the former are divided into basic and acid groups. If the dye is soluble, a strong solution (10 to 20 grms. per litre) is prepared and filtered, and a portion tested with a solution containing 10 grms. of tannic acid and 10 grms. of sodium acetate in 100 cc. of water (see p. 450). A few drops of this reagent are sufficient, and it is necessary to heat in order to complete the reaction, since certain sulphonic acid derivatives of triphenylmethane give at first precipitates, which, however, dissolve when the temperature is raised.

Weingaertner's tables, with some additions, are given on pp. 831-833. The figures in parentheses refer to pages in this work where further information regarding the characteristics of the dyes may be found.

Observations (Table I.) After having reduced the basic colouring matter with zinc powder and hydrochloric acid, the liquid must be immediately filtered, and as quickly as possible. It is very important to neutralise the hydrochloric acid in the filtered liquid with sodium acetate, since mineral acids in excess may form with the basic colour acid salts, whose colour is different from the normal salts.

The primitive shade does not appear on oxidation in the colouring matters in column F, but in certain cases oxidation produces different shades from the primitive. When Bismarck-brown and chrysoidine are reduced the di- and tri-amines are found, which easily oxidise in the air to a brownish-red colour. It is very important to know how to distinguish this shade from the original shades, which are brown or yellow. After reduction and oxidation methylene-green gives a blue shade.

The oxidation of the reduced solution on the filter paper may be facilitated by gently heating. Some colours oxidise with such rapidity that the original colour returns whilst filtering.

(Table II.).—(a) The reduction of the acid yellow, orange, scarlet, or claret non-fluorescent colours requires special precautions. The best way is to treat with zinc powder and hydrochloric acid, and afterwards to neutralise with sodium acetate, as has already been pointed out. The reduction of the group NO_2 , which some colours contain, will often be too slow if ammonia or acetic acid is used.

(b) It is necessary, as before, to compare with great care the original colour with that which is produced by re-oxidation, so that their

TABLE I.
ARTIFICIAL COLOURING MATTERS SOLUBLE IN WATER.

The Aqueous Solution gives a Precipitate with the Tannin Reagent.

BASIC COLOURING MATTERS.

The Aqueous Solution is reduced by Zinc Powder and Hydrochloric Acid, Neutralised and Filtered.

The original shade reappears.					The original shade does not reappear.
Red.	Yellow or Orange.	Green.	Blue.	Violet.	
Magentas (457). Toluylene-red (463). Safranines (464). Rhodamines (564).	Phosphine (468). Benzoflavine (469).	Malachite-green (473). Brilliant-green (476). Victoria-green (476). Methyl-green (471).	Methylene-blue (482). New-blue (484). Muscarine (485). Nile-blue (486). Paraphenylene-blue (491). Toluylene-blue (492).	Methyl-violet (494). Hofmann's violet (494). Mauveine (498). Giroflé (466). Crystal-violet (495).	Chrysoidine (467). Bismarck-brown (499). Auramine (470). Victoria-blue (480). Methylene-green (477).
A	B	C	D	E	F

TABLE II.
ARTIFICIAL COLOURING MATTERS SOLUBLE IN WATER.
The Aqueous Solution does not give a Precipitate with the Tannin Reagent.

ACID COLOURING MATTERS.

The Aqueous Solution is reduced by Zinc Powder and Hydrochloric Acid or Zinc Powder and Ammonia and Filtered.

The solution is decolorised.			The solution becomes brown-red. The colour of the ammoniacal solution reappears in the paper.
The original colour reappears on paper.			
The aqueous solution is acidulated with hydrochloric acid, and treated with ether.	The colouring matter, heated on platinum foil		
	Burns quietly, or slightly deflagrates, giving off coloured vapours.		
The ether dissolves the colouring matter, and the solution immediately becomes colourless.	Heat a piece of calico, not mordanted, in the aqueous solution.		
	The colour does not resist warm soaping.		
Eosins (556). Aurin (566). G	Sulphonated rosanilines (539). Sulphonated indulin (551). H	Tetrazo- (Congo-) colours (406-446). J	Acid azo-colours (512-533). Tartrazin (541). Erythrosin (562). K
	Nitrated colouring matters (nitrophenols — nitrated amines) (509-512). I		

TABLE III.
ARTIFICIAL COLOURING MATTERS INSOLUBLE (OR SPARINGLY SOLUBLE) IN WATER.
The Colouring Matter is treated with Water and some drops of a 5% Soda Solution added.

It dissolves.	It does not dissolve.			
	The colouring matter is heated with 70% alcohol.			
The alkaline solution is filtered, treated hot, with zinc powder, then poured on a filter paper.	It is dissolved.			
	The alcoholic solution is not fluorescent. Add a little 33% soda solution.			
The colour of the alkaline solution reappears.	The colour does not change.			
	The colour changes to red-brown.			
The colour of the alkaline solution reappears.	The colour changes to red-brown.			
	The colour changes to red-brown.			
M	N			
	O			
M	P			
	Q			
M	R			
	S			

identity or difference may not be mistaken. In the reduction of nitro- or azo-bodies the diamines or amidophenols are formed, which by oxidation give dirty or brown shades. In the column K it equally applies to erythrosin, for, when reduced, iodine is separated and fluorescein formed.

(c) All the colouring matters not specified in (a) are reduced by zinc and ammonia.

(d) When the acid colours are being reduced, the solution, as long as zinc powder is present, should be colourless, or at most slightly yellow or red.

(e) The nitro-derivatives of fluorescein and the azo-colouring matters can be easily recognised, since on heating a quantity on platinum foil "Pharaoh's serpents" are formed.

(f) In order to detect the group NO_2 in some of the yellow colouring matters (e.g., picric acid), a little sodium carbonate should be added before heating on platinum.

(g) It is very difficult to completely reduce alizarin S. It is therefore put in column L. The colour of the ammoniacal solution more often returns, but if the reduction has been carried too far that colour does not re-appear.

Having found the group to which the colouring matter belongs, small portions may be tested with special reagents, and the results compared with the reactions given by the various colouring matters on pp. 404 to 666; or small pieces of cotton or wool may be dyed, and the reactions compared with the tables (pp. 840 to 873).

A valuable paper on the "Qualitative Analysis of Colouring Matters," by O. N. Witt, is given in the *Journal of the Soc. of Dyers and Colourists*, 1886, pp. 45-64.

EXAMINATION OF FIBRES, YARN, AND CLOTH.

The characteristics of the various fibres have been given under the headings *Cotton, Linen, &c., Wool, and Silk* (pp. 11 to 57). The fibres are best distinguished from each other by means of the microscope. Vegetable fibres may be readily distinguished from animal fibres by the smell on burning, and by the action of caustic alkalies. Of the animal fibres, wool becomes brown or black when gently warmed in a solution of plumbite of soda, whereas silk is not altered in colour. Silk may be further distinguished from wool by its solubility in a solution of chloride of zinc.

Estimation of Silk, Wool, and Vegetable Fibre and Size and Finish in Fabrics.—The following method is taken from the *Journal of the Society of Dyers and Colourists* (1884, p. 46):—

Four pieces of the fabric, each weighing 2 grms., are taken, one of which is put on one side. The other three are boiled for a quarter of an hour in a 3 per cent. solution of hydrochloric acid. If the liquid is strongly coloured, the boiling is repeated with a fresh quantity of acid. The pieces of cloth are then well washed and wrung, and one of them put on one side. In this manner the fabric is freed from size

and dressing, and the dye is more or less removed. [If silk is present and it is heavily weighted, a portion of the fabric should be ignited and the ash determined, since the whole of the material used for weighting may not be removed.] Two of the three pieces, after the treatment with acid and washing, are immersed for one or two minutes in a solution of basic chloride of zinc of 1.65 sp. gr. This is prepared by dissolving 1000 parts of chloride of zinc and 40 parts of zinc oxide in 850 parts of water. The patterns are allowed to drain, and washed, first in acidulated water, and then in pure water. By wringing the patterns after each immersion in a piece of linen the operation is accelerated, and the silk is thus completely removed. One of these patterns is laid on one side, and the other gently boiled for a quarter of an hour in a 5 per cent. solution of caustic soda, and afterwards carefully washed. The four patterns are then immersed in warm distilled water for a quarter of an hour, wrung out, dried in a water-oven, and exposed to the air. The following day the pieces are weighed. The first piece should weigh 2 grms., and any difference not exceeding 5 milligrammes may be neglected, but a greater difference must be taken into account. The difference in weight between the first and the second patterns represents size and dressing; that between the second and third represents the weight of silk; that between the third and fourth gives the weight of wool, whilst the weight of the fourth gives the amount of vegetable fibre present. Since the vegetable fibre is attacked somewhat by the caustic soda, it is usual to make an allowance of 5 per cent. It is, however, unnecessary to use such a strong solution of caustic soda as given above; a 2 per cent. solution is sufficiently strong to remove the wool, and the action upon the cotton or other vegetable fibre is thereby much reduced.

Fabrics and yarn composed of two fibres (cotton and wool, wool and silk, cotton and silk) are much more common than those with three, when, of course, one of the above operations is omitted.

In many cases the cotton and wool in mixed goods may be determined by carefully separating the weft and the warp threads and weighing the fibres thus obtained.

Estimation of Water.—The conditioning of textile fibres and fabrics has been already referred to under *Wool*, and *Silk* (pp. 37 and 50); but it is frequently necessary to operate upon smaller samples of material than are suitable for the apparatus in general use for that purpose. The following method, which has been devised and used by Rawson, gives very good results. The quantity of material used for the operation is from 5 to 10 grms. The loose material, yarn, or cloth is weighed out and introduced into a thin glass tube of special construction. The body of the tube is about 6 inches in length and 1 inch in diameter. One end is fitted with a ground glass stopper (as in an ordinary filter tube), and the other is connected with a short piece of open tubing about $\frac{1}{4}$ inch in diameter and 2 inches in length.

The stopper is removed and the tube inserted by means of a cork into a tubular water-bath. A current of dry air is drawn through the tube by means of an aspirator, whilst the water in the bath is kept boiling. In the course of 30 to 45 minutes the glass tube with its contents is removed from the bath, the stopper is inserted, and the small open end connected, by means of a short piece of rubber tubing, to a calcium chloride tube. When cold, the tube containing the dry fibre is weighed, the loss in weight being water. If desired, the tube may be again heated in a current of air, but it is seldom that a further loss takes place. The operation is completed in a shorter time if a temperature of 105° to 110° be employed instead of that of boiling water. This temperature may be conveniently obtained by using a mixture of glycerin and water. The bath (especially if glycerin or any other substance in addition to water be used) should be provided with an upright condenser. The bath can, of course, be made to accommodate half a dozen or more tubes, if desired.

Estimation of Oil.—Oil and grease in fabrics, &c., are most conveniently determined by extraction with a volatile solvent, such as ether or carbon disulphide, in a Soxhlet's apparatus. From 2 to 5 grms. of the material are taken and introduced into the body of the tube. The lower extremity of the apparatus is connected with a small wide-mouthed flask (previously weighed dry) containing 50 to 70 cc. of ether (or other solvent), and the upper end is connected to an inverted condenser. The flask is arranged to rest on a water-bath, under which is placed a small flame. The heat is so regulated that the ether distils and syphons over into the flask at the rate of about twelve times per hour. When the extraction is complete, the material is removed and the solvent recovered. The flask is then heated for about 30 to 40 minutes in a water-oven, allowed to cool, and weighed.

Estimation of Mineral Matter (metallic oxides as mordants, &c.).—The total mineral matter is determined by burning 5 to 10 grms. of the material in small portions at a time in a platinum dish and igniting until all the carbon has disappeared. As the ash is usually very light, great care must be taken to prevent any portions being carried away by currents of air. The dish, on cooling, is then weighed. On p. 363, under *Logwood*, short methods are given for the detection of metallic oxides in the ash of fabrics. A brief description will now be given of the quantitative determination of a few of these oxides.

Estimation of Chromium.—The ash from about 5 grms. of material is mixed with ten to twelve times its weight of a mixture of two parts of potassium chlorate and three parts of sodium carbonate, and fused for 15 to 20 minutes in a platinum crucible. On cooling, the mass is treated with hot water and filtered, the residue being well washed with hot water. The filtrate and washings are poured into a porcelain basin, treated with a considerable excess of sulphuric acid and a known weight (in slight excess) of pure ferrous ammonium

sulphate. The excess of ferrous iron is then titrated with $\frac{N}{10}$ potassium bichromate, as given on p. 772. One part of ferrous ammonium sulphate consumed (after deducting excess) = $\cdot 065 \text{ Cr}_2 \text{O}_3$ or $\cdot 0854 \text{ CrO}_3$.

Estimation of Iron and Copper.—If chromium is present, the residue, after fusing and treating with water, is dissolved in hydrochloric acid. If chromium is absent, the ash is dissolved direct in hydrochloric acid; in some cases the addition of a little nitric acid is also necessary. The acid solution is diluted with a little water and an excess of ammonia added. The ferric oxide is collected on a small filter, washed a little, redissolved in hydrochloric acid, and reprecipitated by ammonia. The ferric oxide, which will now be free from copper, is dissolved in hydrochloric acid and titrated colorimetrically, either with ferrocyanide or thiocyanate, as given on p. 752.

The copper in the filtrate and washings is estimated by "colour titration" in the following manner:—The ammonia is carefully neutralised with acetic acid (a very slight excess of acetic acid may be present) and the liquid made up to a known volume. The ammonia may also be removed by boiling, but in some cases a portion of the copper is thereby precipitated. The addition of acetic acid is preferable, but care must be taken not to add more than a very slight excess. A measured volume of the neutralised solution is run into a Nessler glass, half a cc. of a 5 per cent. solution of potassium ferrocyanide, and 5 cc. of a 10 per cent. solution of ammonium nitrate are added, and the liquid diluted to 100 cc. The depth of shade produced is compared with that given by a standard solution of copper treated in exactly the same manner in another Nessler tube. The copper solution is prepared by dissolving $\cdot 393$ gm. of pure crystallised copper sulphate in a litre of water. 1 cc. of this solution = $\cdot 0001$ gm. of Cu.

Detection and Estimation of Arsenic in Textile Fabrics, &c.—The following method, worked out (with modifications) from the papers named below,* can be recommended:—

About 20 grms. of fibre, yarn, or cloth are cut up and introduced into a stoppered retort of about 500 cc. capacity. The neck of the retort is bent at an obtuse angle, and arranged so that the portion nearest the body points slightly upwards and the bent portion slightly downwards. The retort is connected to a Liebig's condenser, the inner tube of which at the extremity farthest from the retort is bent straight down through a cork into a receiving flask capable of holding about 600 cc. About 100 cc. of water are placed in the flask, which is immersed in a basin of cold water. A small set of bulbs (nitrogen bulbs) containing a little water is attached to the flask. 200 cc. of pure hydrochloric acid are poured into the retort, and after standing an hour, 5 cc. of a saturated solution of pure ferrous chloride added,

* A. Atterberg, *Journ. Chem. Soc.*, 1886, Abs. p. 100; Fresenius and Hintz, *Journ. Soc. Chem. Industry*, 1888, p. 456; *Journ. Soc. Dyers and Col.*, 1888, p. 131; Chittenden and Donaldson, *Chem. News*, vol. xliii. (1881), p. 21.

and the liquid distilled down to a small bulk. For this purpose an oil-bath should be used. The retort is allowed to cool, when 50 cc. more of hydrochloric acid are added and again distilled. The distillate is then made up to a known bulk, and one-half or one-fourth of the solution treated in a Marsh's apparatus.

For this purpose 25 to 30 grms. of pure zinc rods are immersed in a solution of platinum chloride for a few minutes and well washed with water. The platinised zinc is introduced into a flask of a capacity of about 250 cc., having a horizontal side-tube attached to the neck. This is connected to a chloride of calcium tube, into which is fixed a piece of hard glass tubing about 12 inches in length and a quarter of an inch in diameter. The hard glass tube is drawn out near the end and bent upwards. The flask is provided with a tapped funnel, into which is placed a little dilute pure hydrochloric acid, and allowed to flow on to the zinc. When the air has been driven out of the apparatus the jet is lighted and the hard glass tube (protected with wire gauze) heated to redness for a space of 6 or 8 inches by means of a small furnace of four or five Bunsen burners. An aliquot part of the distillate (50 to 150 cc.) containing the arsenic in the form of arsenious acid is poured into the funnel and allowed to drop regularly into the flask at the rate of about 60 cc. per hour. Arseniuretted hydrogen is formed which, on passing through the red-hot tube with excess of hydrogen, is decomposed and arsenic is deposited. If the amount of arsenic is considerable, a space of 2 or 3 inches should be left between the heated portion and the drawn-out part of the tube. If very small, the tube should be heated close to the drawn-out part so that the arsenic may be deposited in the narrow portion. When the acid liquid containing the arsenic has passed into the flask, 10 to 20 cc. of pure hydrochloric acid are added and allowed to slowly flow in as before. The tube is then allowed to cool, when the portion containing the deposit of arsenic is cut off with a sharp file and carefully weighed on a delicate balance. The arsenic is then removed by simply heating the tube which, after cooling, is again weighed. The difference between the two weighings gives the amount of arsenic present in the solution. In many cases the arsenic mirror may be too small to weigh, and yet it may represent a considerable amount (comparatively speaking) of arsenic. In such cases the amount of arsenic may be approximately estimated by making experiments with known quantities (very small) of arsenic, and comparing the mirrors obtained. Before commencing the examination for arsenic, it is absolutely necessary to make blank experiments with all the substances used in order to ascertain whether they are quite free from arsenic or not.

Identification of Dyes on the Fibre.—When one colouring matter only has been applied to a fabric it may usually be detected and recognised with comparative facility. In practice, however, shades are more frequently obtained by a combination of two or more colour-

ing matters, when the difficulties of detection are much increased. The characteristic reactions of certain dyes on the fibre are sometimes altogether obscured by the presence of very small quantities of other dyes which produce deep colourations with the various reagents employed. The reactions of a considerable number of artificial and natural dyes on cotton and wool are given in the following tables, and in the case of the natural dyes further particulars are given under the respective colouring matters. In testing a bit of dyed material, and comparing the reactions obtained with the tables, a piece of white yarn (cotton, wool, or silk, mordanted, if necessary) should be dyed with the suspected colouring matter as near as possible to the same shade. The two pieces—that dyed with the known colouring matter, and the sample—are then tested side by side with the same reagents under identical conditions. In this way, and in this way only, the conclusions arrived at from the tables are confirmed or otherwise. In many cases, especially with compound shades, much information may be gained by ascertaining whether the material has been mordanted, and if so, what mordant is present. Methods for detecting the principal mordants are given on p. 363. If no mordant is present, a great number of colouring matters are excluded. If found to be mordanted, both classes of dyes may be present. The constituent dyes of a compound shade may in many cases be ascertained by heating the material with various solvents, such as alcohol, ammonia, a weak solution of carbonate of soda, dilute hydrochloric or sulphuric acid, &c. The solutions are then neutralised (when necessary) or in some cases slightly acidulated, and small pieces of cotton, wool, or silk dyed in the liquid under various conditions. The dyed fibres are dried and tested according to the methods given in the tables, and compared with material dyed with known colouring matters. Characteristic reactions are often obtained by boiling the fabric with a 5 per cent. solution of sulphuric acid, and then adding an excess of caustic soda to the liquid, as well as immersing the boiled piece of material in caustic soda. The test is especially of value for logwood, alizarins, and mordant-dyes in general. In other cases information may be gained by boiling with a weak solution of sodium carbonate, and adding an excess of acid to the liquid. Benzidine-dyes in mixtures or compound shades may generally be recognised by boiling the material in an alkaline solution with a small piece of white cotton. The cotton, which takes up a portion of the colouring matter, is dried and tested with the various reagents.

A useful series of tables for detecting dyes on silk is given by B. Martinon in the *Journ. of the Soc. of Dyers and Colourists*, 1887, p. 124.

In the following tables the several reagents are applied in the cold, unless otherwise stated. Small pieces of the dyed material are placed in porcelain basins, and about 1 cc. of the reagent added in each case. Where concentrated sulphuric acid and hydrochloric acid are used, characteristic reactions are sometimes obtained by diluting with water. Except where otherwise stated, the reactions refer to dyes on wool.

BLACK, VIOLET, AND

COLOURING MATTER.	Concen. H_2SO_4 .		10% Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Logwood (on chrome mord.)	Olive-brown	Yellow	Violet	...	Red-violet (slowly)	Red-violet
Logwood (on iron mord.)	Yellowish-brown	Yellow	Dull purple	Light red	Crimson	Crimson
Wooded black (see p. 354.)	Dirty red-brown	Dirty greenish-yellow, green on dilution	Little change	...	Redder	Crimson
Naphthol black B (Cas.)	Dark bluish-green	Greenish-blue	Little change	...	Little change	...
Naphthol black 3 B (Cas.)	Dark bluish-green	Greenish-blue
Naphthol black 6 B (Cas.)	Greener	Greenish; bluish-violet on diluting	Redder	Colourless
Naphthylamine black D (Cas.)	...	Blue-black; red-violet on diluting	Little change	...	No change	Light green
Anthracite black D (Cas.)	Greener	Greenish-grey	Little change	...	Violet	...
Wool black (B.A.S.F.)	...	Deep blue; violet on diluting	Brownish-purple	Dirty brown
Brilliant black B (B.A.S.F.)	Greener	Greenish-blue; violet on diluting	Little change	...	Slightly redder	Colourless
Victoria black 5 G (By.)	...	Dirty green	Greener	Colourless
Victoria black blue (By.)	...	Bluish-green
Jet black R (By.)	Deep blue	Deep blue	Little change	...	Little change	Faint green
Wool grey (M.L.B.)	Dirty light maroon	Dirty grey	Greyish-violet	..	Lighter	Brownish-maroon
Diamond black (chrome mord.) (By.)	Greener	Bluish-green; on diluting violet	Dark bluish-green	...
Alizarin black (chrome mord.) (B.A.S.F.)	Little change	Dirty grey	Little change	Dirty pink

BLUE COLOURS.

HNO ₃ Sp. Gr. 1.42.	SnCl ₂ + HCl.	10% Sol. NaHO.		NH ₄ HO Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Orange spot with red rim	Purple and then brown	Violet	Violet	Slowly violet	...	No action
Yellow-orange spot	Purple and then brown	Violet	Violet	Slowly violet	...	No action
Yellow spot, red rim	Little change	Redder	...	Redder	...	Blue on boiling ; colour deposited on cooling
Red spot	Dull crimson	Little change	...	Bluish-violet	Violet	...
Red spot	Crimson	Bluish-violet	Violet	...
Red spot	Dark purple	Light blue	...
Brown spot	No change	Bluer	Blue	...	Light reddish-violet	Red-violet on boiling
Greenish-yellow spot, brown rim	Deep red-dish-violet	Little change	Pink	Violet on boiling
Yellow spot, red rim	Light olive-brown; after standing colourless	Dark violet on standing	Violet	Reddish-violet on boiling
Orange-red spot	Light red	Little change	Light blue	Blue-black on boiling
Dirty-red spot	Decolorised	Dark green	Green	...	Blue-violet	...
Red-yellow spot, red rim	...	Greener	Dirty violet	...	Reddish-violet	...
Yellow spot, red-brown rim	Lighter; finally decolorised	Dark green	...	Little change	...	Violet-green
Greenish-yellow spot, green rim	Violet	Light dull brown	...	Dull brown	...	Light violet
Dull red spot	...	Darker	Bluish-grey	...	Bluish-grey	Violet
Olive-brown spot	Dirty olive-yellow	Dark greenish-blue	...	Greenish-blue

COLOURING MATTER.	Concen. H ₂ SO ₄ .		10% Sol. H ₂ SO ₄ .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Fast violet red shade (By.)	Dark slate-blue	Blue	Brighter	...	Bluer	Slightly blue
Fast acid violet 10 B (By.)	Green; changing to greenish-yellow	...	Bright bluish-green	...	Bright green; changing to amber-yellow	...
Acid violet B B (B.A.S.F.)	Dull yellow	Yellow	Greenish-yellow	...
Acid violet 6 B (By.)	Orange	Yellow	Orange-yellow	Light yellow
Acid violet 4 B N (B.A.S.F.)	Yellow	...	Brighter	...	Bright yellow	Yellow
Acid violet 4 R S (B.A.S.F.)	Dull yellow	Yellow	Brighter	...	Almost decolorised	...
Acid violet 5 R S (B.A.S.F.)						
Formyl violet 4 B S (Cas.)	Orange-yellow	Yellow	Bluer	...	Orange-yellow	Light yellow
Chrome violet (chrome mord.) (By.)	Orange-yellow	Yellow	Bright crimson	Pink
Alkali violet (B.A.S.F.)	Bright orange	Yellow	Bluish-green	...	Bright orange	Yellow
Azarin (chrome mord.) (M.L.B.)	Deep crimson	Deep crimson
Gallocyanin (chrome mord.) (Durand)	Bluer	Deep blue; pink on dilution	Little action	Faint violet	Violet	Violet
Alizarin cyanin R (chrome mord.) (By.)	Deep red-dish-blue	Deep blue; violet on dilution	Darker	...	Redder	Light blue
Alizarin blue S W (chrome mord.) (B.A.S.F.)	Greener	Deep greenish-blue	No change	...	Redder	Light red
Alizarin indigo blue (chrome mord.) (B.A.S.F.)	Darker	Dark red-dish-blue	Slightly darker	Pink
Indigo blue (vat dyed)	Olive-green	Olive-green; blue on dilution	No change	...
Indigo extract	Olive-grey; blue on dilution	Grey	No change	...	Duller	Light blue
Methyl violet B (B.A.G.)	Orange; restored on dilution	Yellow	Bluish-green	Greenish-blue	Orange; restored on dilution	Yellow

Blue Colours—*Continued.*

HNO ₃ Sp. Gr. 1.42.	SnCl ₂ + HCl.	10 % Sol. NaHO.		NH ₄ HO Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Orange-red spot, blue rim	Dull red	Blue	Faint violet	Little change	...	Little action
Green spot, greenish-yellow rim	Light blue	Light blue
Yellow spot, greenish-blue rim	Bluer	Almost decolorised	...	Decolorised	...	Light violet
Yellow spot, light green rim	Peacock- green	Decolorised	...	Lighter colour; re- stored on exposing to the air	...	Light violet
Yellow spot, greenish rim	Peacock- green	Decolorised	...	Decolorised; colour re- stored on exposure to air	...	Violet
Bright yellow spot	Little or no change	Decolorised	...	Decolorised	...	Red-violet on standing
Yellow spot	Bright green	Nearly decolorised	...	Lighter	...	Light violet on boiling
Yellow spot, red rim	...	Lighter on standing	...	Lighter	...	Light red violet
Yellow spot	Bluish-green	Colourless	...	Colourless	...	No action
Dark red-brown spot	Slightly brighter	Deep reddish- blue in the cold
Red-brown spot	...	Dirty purple	No action
Dirty green spot	Redder	Greener	Slightly bluish-red
Yellow spot, violet rim	Dark dull violet	Bluish- green	Colourless	Little change	...	Little or no action
Dirty yellow spot, violet rim	...	Greener	Colourless	Greener
Yellow spot, green rim	No change	No change	...	No change	...	Light blue on boiling
Yellow	Slowly decolorised	Yellow	Yellow	Green	Light yellow	No action
Yellow spot, with green and orange rim	Bluish-green	Slowly decolorised	...	Nearly decolorised	..	Reddish-violet

COLOURING MATTER.	Concen. H_2SO_4 .		10 % Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Methyl violet 6 B (Berlin)	Orange; on diluting bright blue	Yellow; on diluting light blue	Greenish-blue	...	Orange	Yellow
Crystal violet 6 B (B.A.S.F.)	Orange; on diluting green to violet	Yellow; on diluting green	Dark-green	...	Orange	Yellow
Ethyl purple (B.A.S.F.)	Orange; on diluting green to violet	Yellow; on diluting yellow	Dark olive-green	Yellow	Orange	Yellow
Regina violet (Berlin)	Brown	Dirty brown	Bluer	...	Dark grey	Light brown
Fast violet, blue shade (By.)	Dark green	Dark green	Brighter	...	Dark bluish-green	...
Toluidine blue (M.L.B.)	Dark olive-green	Greenish	...	Light blue	Little or no change	Blue
Basle blue (Durand)	Olive-green	Yellow	Redder; blue on dilution	Reddish-violet
Thiocarmin R (Cas.)	Dark green	Dirty green; blue on dilution	Bluish-green	Bluish-green
Patent blue (superior) (M.L.B.)	Greener; changing to dirty yellow	...	Bright emerald-green	...	Bright yellowish-green; changing to amber-yellow	Light yellow
Neutral blue (Cas.)	Orange	Yellow	Bright green	...	Bright orange	Yellow
Alkali blue 4 B (Cas.)	Bright red	Brownish-red	No change	...	Redder	Light green
Pure soluble blue (Cas.)	Dull red	Red	No change	...	Brighter	Light blue
Victoria blue B (B.A.S.F.)	Red; restored on dilution	Red	No change	Yellowish	Red; restored on dilution	Red
Victoria blue 4 R (B.A.S.F.)	Red; restored on dilution	Red	No change	...	Red; restored on dilution	Red
Cyanin B (M.L.B.)	Green; changing to dirty yellow	...	Bright greenish-blue	...	Bright greenish-blue; changing to yellow	...
Chrome blue (By.)	Crimson	Dirty maroon	Crimson	Pink
Induline N N (B.A.S.F.)	Lighter and redder	Blue; violet on dilution	Little change	...	Brighter	Light blue

Blue Colours.—*Continued.*

HNO_3 Sp. Gr. 1.42.	$\text{SnCl}_2 + \text{HCl}$	10% Sol. NaHO .		NH_4HO Sp. Gr. .890.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Yellow spot	Blue	Much lighter	Colourless	Much lighter	Colourless	Violet
Yellow spot, darker rim	Dark green	Lighter	...	Lighter	...	Violet
Yellow spot, orange rim	Green	Bluer	...	Bluer	...	Violet
Yellow spot, bluish-green rim	Much bluer	Decolorised (dirty brown)	...	Decolorised	...	Light red-violet on boiling
Orange-red spot, bright greenish-blue rim	Dull red	Reddish-blue
Olive-green spot	Decolorised	Dull crimson	Blue
Bluish-red spot	Brighter	Darker	...	No change	Light blue	Deep red-blue on boiling
Green spot, lighter rim	Slightly greener	Darker	...	Slightly darker	...	Light bluish-green
Bright yellow spot, green rim	Bright green at first; slowly light yellow	Greener	Light blue	Little change	Colourless	Little action
Green spot, with yellow-orange rim	Green	Much lighter	...	Lavender	...	Reddish-violet on boiling
Green spot, dark rim	...	Purplish-brown	...	Decolorised	Light blue	Blue
Green spot	Little or no change	Light brownish-red	...	Decolorised	...	Blue
Greenish-yellow spot, red rim	Darker	Dark maroon	Colourless	Dirty violet	Colourless	Blue in cold
Greenish-yellow spot, brown rim	...	Reddish-violet	...	Little or no change	...	Blue in cold
Yellow spot, bright green rim	...	Olive-green	...	Brighter	Faint blue	Faint greenish-blue
Greenish-yellow spot	Slightly greener	Bright blue
Dark violet	Little change	Reddish-violet	Colourless	Little or no change	Colourless	Bluish-violet

Black, Violet, and

COLOURING MATTER.	Concen. H_2SO_4 .		10% Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Nigrosine (spirit sol.) (B.A.S.F.)	Dark greenish-slate	Dark grey	No change	...	Dark slate	...
Nigrosine (Berlin)	Dark violet	Blue	Darker	Reddish-blue
Indazine (Cas.)	Dirty dark green	...	Little change	Faint red-dish-blue	Darker	Blue
Metaphenylene blue (Cas.)	Dirty grey	Blue
Paraphenylene blue (Dahl.)	Darker	Blue	Darker	Blue
Indamine blue B (paste) (M.L.B.)	Much darker	Bright blue	Darker	...	Darker	Bright blue
Indoin blue (B.A.S.F.)	Dirty olive-green; on diluting blue-violet	Olive-green	Bluish-green	Slate
Methylene blue 4 B (B.A.S.F.)	Olive-green	Green	Little change	Light blue	Lighter	Blue
Night blue (B.A.S.F.)	Red	Red	Green	Yellow	Bright red	Red
Nile blue (B.A.S.F.)	Red	Brown	Greener	Light yellow	Greenish-yellow	Greenish-yellow
Naphthylene blue R (extra) (cotton)	Dark blue to green	...	No change	...	Dark blue	...
Benzo black blue (cotton)	Green	Slightly blue	No change	...	Greener	Colourless
Benzo black S (extra) (cotton)	Dark violet	Violet	Greener	Colourless	Dark violet	Colourless
Benzo blue black R (cotton)	Greenish-blue	Blue	No change	...	No change	...
Violet black (cotton)	Deep blue	Blue	Little change	...	Bluer	Colourless
Azo-violet (cotton)	Greenish-blue	Blue	Blue	Colourless	Blue	Colourless
Heliotrope 2 B (cotton)	Violet	Violet	Little change	...	Bluer	Colourless
Azo-mauve N (cotton)	Greenish-blue	...	Lighter	...	Blue	...
Benzo grey S (extra) (cotton)	Dark violet	Greenish-blue	Green	Colourless	Bluer	Colourless

Blue Colours—*Continued.*

HNO_3 Sp. Gr. 1.42.	$\text{SnCl}_2 + \text{HCl}$	10% Sol. NaHO .		NH_4HO Sp Gr. '880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
...	...	Purplish-brown	...	Brown	Grey	...
...	...	Dirty maroon	...	Maroon
Maroon spot, greenish rim	...	Redder	Violet on boiling
Dull green spot	...	Duller
Greenish-yellow spot	Lighter	Purple	...	Violet
Dull green spot	...	Purple	Blue on boiling
Bright yellowish- green spot	Greener	On standing violet	Pink	Deep blue, in cold
Green spot	Decolorised	Dull bluish- violet	...	Little change	...	No action
Red spot, green rim	Greener	Reddish- brown	...	Grey	...	Blue colour on boiling
Brownish-yellow spot, green rim	...	Deep crimson	...	Dark violet	...	Blue, on boiling; with red fluor- escence
...	Nearly decolorised	Brown	...	Brown	...	Blue
Brownish-red	Decolorised	A little darker	Colourless	No change	...	Little action
Scarlet	Decolorised	Red-violet	Faint red	Red-violet	Pink	Light violet
Light brown	Decolorised	Red-violet	Colourless	Violet	Faint pink	Violet
Red-orange	Decolorised	Little change	Pink	Little change	Violet	Crimson
Light red	Decolorised	Crimson	Colourless	Crimson	...	Red-violet
Red-orange	Decolorised	Crimson	Pink	Little change	...	Little action
...	Decolorised	Redder	...	Slightly redder	...	Violet
Dull scarlet	Decolorised	Red-violet	Colourless	Redder	..	Faint violet

Black, Violet, and

COLOURING MATTER.	Concen. H_2SO_4 .		10% Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Diamine blue B X (cotton)	Greenish-blue	Blue	Redder	...	Violet	Colourless
Diamine blue 3 R (cotton)	Greenish-blue	Blue	No change	...	Darker	Colourless
Azo-blue (cotton)	Greenish-blue	Blue	No change	...	Little change	...
Benzo azurin (cotton)	Greenish-blue	Blue	Redder	Colourless	Little change	...
Benzo azurin G (cotton)	Greenish-blue	Blue	Redder	Colourless	Little change	...
Brilliant azurin 5 G (cotton)	Bluish-green	Light green	Little change	...	Little change	...
Benzo azurin 3 G (cotton)	Greenish-blue	Blue	Little change	...	Darker	Colourless
Sulphonazurin (cotton)	Violet, turning redder	Violet	Little change	...	Dirty violet	Colourless
Diamine blue 6 G (cotton)	Dirty olive grey	...	Little change	...	Little change	...
Benzo black blue G (cotton)	Green	...	No change	...	Little change	...
Diamine black B O (cotton)	Deep blue	Blue	Redder	Colourless
Diamine black B O (developed with phenylenediamine) (cotton)	Deep blue	...	Little change	...	No change	...
Diamine black R O (cotton)	Deep blue	Blue	No change	...	Redder	Colourless
Diamine blue black R O (developed with resorcin) (cotton)	Darker	...	No change	...	No change	...

Blue Colours—*Continued.*

HNO_3 Sp. Gr. 1.42.	$\text{SnCl}_2 + \text{HCl}$	10% Sol. NaHO .		NH_4HO Sp. Gr. .830		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Light brown	Decolorised	Red-violet	Colourless	Violet	Colourless	Faint violet
Orange yellow	Decolorised	Magenta	Pink	Red-violet	Pink	Red-violet
Orange	Slowly decolorised	Magenta	Pink	Red-violet	Pink	Red-violet
Light brown	Slowly decolorised	Crimson	Light pink	Red-violet	Pink	Red-violet
Light brown	Slowly decolorised	Crimson	Light pink	Red-violet	Pink	Violet
Crimson	Slowly decolorised	Red-violet	Colourless	Red-violet	Colourless	Light blue
Orange	Decolorised	Red-violet	Pink	Violet	Pink	Violet
Yellow	Decolorised (rapidly)	No change	...	No change	...	Blue
Yellow	Light violet	Redder	Colourless	Little change	...	Faint blue
Dull red	Decolorised (rapidly)	Little change	...	Little change	...	Faint blue
Violet	Slowly decolorised	Redder	Pink	Little change	...	Faint violet
...	Slowly decolorised	No change	...	No change	...	Faint violet
Violet	Slowly decolorised	Red-violet	Pink	Little change	...	Faint violet
...	Slowly decolorised	No change	...	No change	...	Faint violet

GREEN

COLOURING MATTER.	Concen. H_2SO_4 .		10 % Sol. H_2SO_4 .		HCl Sp. Gr 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Malachite green (Berlin)	Yellow ; green on dilution	Yellow	Darker	...	Bright orange; green on dilution	Yellow
Brilliant green (Cas.)	Red; green on dilution	Red	Lighter	...	Bright yellow; green on dilution	Yellow
Guinea green (Berlin)	Yellowish- brown	Yellowish- green	...
Fast green (bluish; liquid) (B.A.S.F.)	Dirty yellow	Amber yellow	...
Light Green S F (yellowish) (B.A.S.F.)	Orange	Yellow	Brighter	...	Orange	Faint yellow
Light green S (bluish; liquid) (B.A.S.F.)	Red-brown	Dirty yellow	Brown	Light brown
Victoria green (Karl Zimmer)	Yellow; green on dilution	Yellow	Darker	...	Bright orange; green on dilution	...
Azine green (Leonhardt)	Dirty brown	Violet	...
Azo-green paste (By.)	Light brown	Dirty yellow	Light brown	Dirty yellow
Indoine blue 2 B (B.A.S.F.)	Dark green	Green	Bluish-green	Faint yellow
Naphthol green (Cas.)	Olive	Drab	No change	...	Yellow	Yellow
Alizarin green S W (chrome) (B.A.S.F.)	Deep blue	Blue	Slightly bluer	...	Redder	Pink
Diamond green (chrome) (By.)	Bluer	Greenish- blue	Brighter	...	Bluer	Faint yellow
Gambin (iron mord.) (Read Holliday)	Dull olive- green	Brown	No action	...	Olive	Bright yellow
Dioxin (iron mord.) (Leonhardt)	Very dark green.	Greenish- black; yellow on dilution	Darker	...	Dark red- brown	Red-brown

COLOURS.

HNO_3 Sp. Gr. 1.42.	$\text{SnCl}_2 + \text{HCl}$	10% Sol. NaHO .		NH_4HO Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Red spot	...	Decolorised	...	Decolorised	...	Green on boiling
Yellowish-red spot	Yellower	Decolorised	...	Decolorised	...	Green
Reddish-yellow spot	...	Decolorised	...	Decolorised
Greenish-yellow spot	Lighter and greener	Greener	Pale green
Yellow spot, bright orange rim	Brighter	Decolorised	...	Decolorised	...	Light green on boiling
Reddish-yellow spot	...	Decolorised	...	Decolorised
Red spot	Little or no change	Decolorised	...	Decolorised	...	Green on boiling
Brown spot	Brighter	Darker	Green
Yellow spot, orange rim	Much yellower	Much yellower	...	Almost decolorised	...	Bluish-green
Bright yellowish-green spot	Brighter	...	Blue
Orange-red spot	Very slowly decolorised	Brighter	Light olive	Little action	...	Faint blue on boiling
Brown spot, purple rim	Grey	Greener	...	Greener	...	No action
Red spot, green rim	Brighter
Deep red spot, yellow-brown rim	Little change	No action	...	No action	...	Light yellow
...	...	Very dark red-brown	Red	Dark brown	Brown	Greenish-yellow

YELLOW AND

COLOURING MATTER.	Concen. H_2SO_4 .		10% Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Old fustic (chrome mord.)	Dark yellow; changing to reddish-brown	Yellow	Little change	...	Brighter	...
Young fustic (chrome mord.)	Orange; yellow on standing	Yellow	Darker	Yellow
Persian berries (tin mord.)	Brown	Yellow	Little change	...	Very little change	Yellow
Weld (tin mord.)	Darker	Yellow	Lighter and brighter	Yellow
Quercitron bark (chrome mord.)	Greenish-yellow; changing to brown	Yellow	Little change	...	Little change	Yellow
Turmeric	Reddish-brown	Reddish-brown	Terra-cotta; changing to brown	Light red
Chrysoidine R (Cas.)	Yellowish-brown	Yellow	Orange	...	Scarlet	Pink
Fast yellow G (Kalle & Co.)	Bright terra-cotta	Yellow	Orange; changing to bright scarlet on standing	Pink	Scarlet	Red
Brilliant yellow (Leonhardt)	Dark purple	Red	Brownish-yellow	...	Dark purple	Red
Azo-flavin (B.A.S.F.)	Red-violet	...	Darker	...	Red-violet	Crimson
Uranin G (B.A.S.F.)	Greenish-yellow	Greenish-yellow	Lighter	Yellow	Brighter	Yellow
Phosphine (Berlin)	Dirty greenish-yellow	Light yellow	Orange	...	Brighter and lighter	Yellow
Alizarin yellow A (chrome) (B.A.S.F.)	Dark dull yellow	Faint yellow	Little or no change	...
Anthracene yellow (chrome) (Cas.)	Dark dull maroon	Dirty brownish-maroon	Much darker (brown)	...	Very dark purple	...
Galloflavin (chrome) (B.A.S.F.)	Drab	Drab	Little change	...	Greener	Light yellow
Diamond Yellow G (chrome) (By.)	Dark orange-red	...	Light red-brown	...	Dark orange-red	Light yellow

ORANGE COLOURS.

HNO ₃ Sp. Gr. 1.42.	Sn Cl ₂ + H Cl.	10 % Sol. Na H O.		N H ₄ H O Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Dark brown spot	Brighter	Slightly darker	Faint yellow	Darker	Colourless	No action
Brownish-yellow spot	Yellower	Red-brown	Yellow	Orange	Yellow	No action
Yellow spot	Brighter	Browner	Yellow	Browner	Colourless	No action
Light brown spot	Redder	Orange	Yellow	Brown	Colourless	No action
Yellow spot	Little change	Slightly darker	Yellow	Browner	Yellow	No action
Yellow spot	Reddish-brown	Scarlet	Orange	Scarlet	Orange	Yellow; green fluorescence
Orange-red spot	Orange	Deeper	...	Yellower	...	Yellow
Yellow spot, bright red rim	Decolorised	Darker	Yellow	Little action	Yellow	No action
Dark purple spot	Slightly lighter	Bright scarlet	Slightly pink	Scarlet	...	No action
Red spot, purple rim	Lighter	Greener and darker	...	Little or no change	...	No action
Little change	Little change	Orange-yellow	Yellow	Reddish	Deep yellow	Yellow, with strong green fluorescence
Little change	Nearly decolorised	Yellow	...	Little change	...	Yellow
Green-yellow spot	...	Darker	...	Darker
Orange-yellow spot, dark purple rim	...	Darker	...	Slightly darker
Dull yellow spot	Lighter	Slightly darker	Light yellow	Little change	Colourless	No action
Bright orange-red spot	Light red-brown	Slightly darker	...	Slightly darker

COLOURING MATTER.	Concen. H_2SO_4 .		10 % Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Flavazol (Berlin)	Bright scarlet	Orange	Scarlet	...	Crimson	Yellow
Patent fustin (wool yellow, B.A.S.F.) (Wood & Bedford)	Brownish-red	Red	Darker	...	Brownish-red	Faint yellow
Picric Acid	Drab; restored on diluting	On diluting, yellow	Little change	Light yellow	Decolorised	...
Naphthol yellow (Cas.)	Decolorised	...	Lighter	...	Decolorised	...
Naphthol yellow S (B.A.S.F.)	Browner	Colourless	Lighter	...	Decolorised	...
Tartrazin (B.A.S.F.)	Darker	Bright yellow	No change	...	Slightly darker	Yellow
Thioflavine T (Cas.)	Brown; on standing colourless	...	Lighter	...	Decolorised	...
Milling yellow O (Cas.)	Dark crimson; on diluting, yellow	Red (bluish)	Slightly darker	...	Dull crimson	Crimson
Yellow N (Poirrier)	Dirty dull green; on diluting, violet	On diluting, violet	Maroon	Violet	Red-violet	Red-violet
Tropaeolin O O (Cas.)	Dark blue-violet	Violet	Darkmaroon	...	Dark red-violet	Deep red-violet
Quinoline yellow (B.A.S.F.)	Dull red-yellow	Faint yellow	Amber-yellow	Faint yellow
Metanil yellow (Oehler)	Dark purple	...	Brownish-red; changing to purple	...	Bright purple	Reddish-purple
Aurantia (Berlin)	Decolorised	...	Lighter	...	Decolorised	...
Orange G (Read Holliday)	Crimson	Red	Little change	...	Scarlet	Pink
Orange G T (By.)	Bright crimson	Crimson	Bright red	Pink
Orange R (Bindschedler)	Crimson	Red	Scarlet	Pink
Orange II. (Poirrier)	Bright scarlet; changing to crimson	Scarlet	Scarlet to crimson	Pink
Crocein orange (By.)	Orange-yellow	Red	Brighter	...	Red	Red
Methyl-orange	Crimson	...	Crimson	...	Crimson	Pink

Orange Colours—Continued.

HNO ₃ Sp. Gr. 1.42.	SnCl ₂ + HCl	10% Sol. NaHO.		NH ₄ HO Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Bright scarlet spot	Scarlet	No change	...	No change
Dull red spot	Terra-cotta	Dark brown	Light brown	Dark brown	Light brown	...
Straw-yellow spot	Lighter	Orange	Yellow	Orange	Yellow	Yellow on boiling
...	Decolorised	Little change	Yellow	Paler	Yellow	Yellow on boiling
Browner	Decolorised	Little change	Yellow	Brighter	Yellow	Little or no action
Orange	Lighter; slowly decolorised	Redder	Bright yellow	Brighter	Light yellow	No action
...	Brighter	Much lighter; colourless on standing	...	Lighter	...	Greenish-yellow on boiling
Red spot, deep maroon rim	Decolorised	Brighter	...	Faint yellow
Yellow spot, orange rim; outer rim maroon	Brighter	...	Faint yellow
Red spot, maroon rim	Darker	Brighter	...	Brighter	...	Bright amber yellow
...	Slightly brighter	Duller	...	No change	...	Greenish-yellow on boiling
Red spot, purple rim	Brown; changing to purple	Brighter	...	Little change	...	Faint yellow
...	...	Orange-red	...	Orange	...	Yellow on boiling
Yellow spot, red rim	Decolorised	Terra-cotta	...	No change
...	...	Darker
Yellow spot, red rim	...	Terra-cotta
Yellow spot, scarlet rim	...	Dull scarlet	...	Darker	Light orange	Light orange
...	Decolorised	Browner	...	Slightly darker
Yellow spot, crimson rim	...	Little or no change	...	No change	...	Light yellow on warming

COLOURING MATTER.	Concen. H_2SO_4 .		10% Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Cloth orange	Dark violet	Deep violet	Darker	...	Dark-violet	...
Alizarin orange W (chrome) (B. A. S. F.)	Darker	Light brown	Little change	Slightly darker	Lighter	Yellow
Alizarin orange S (chrome) (By.)	Darker	Light brown	Little change	Darker	Light yellow	Yellow
Thioflavine T (cotton)	Light olive-green, then nearly decolorised	...	Darker	...	Nearly decolorised	...
Benzoflavine (cotton)	Much lighter	...	No change	...	Orange	...
Chrysamin G (cotton)	Crimson	Reddish-violet	Paler	...	Dull crimson	Colourless
Brilliant yellow (cotton)	Red-violet	...	Paler	...	Reddish-blue	Colourless
Hessian yellow (cotton)	Crimson	...	Paler	...	Grey	...
Thioflavin S (cotton)	Light red	Colourless	Orange	Colourless	Lighter	Yellow
Primuline (cotton)	Duller	Light yellow	Orange	...	Orange	Yellow
Primuline (developed with resorcin) (cotton)	Crimson	Red	Redder	...	Dark red	Red
Chrysamin R (cotton)	Red-violet	...	Lighter	...	Blue-violet	...
Thiazol yellow ₁ (cotton)	Brown	Colourless	Orange	Colourless	Orange	...
Carbazol yellow (cotton)	Dark greenish-blue	Blue	Olive-green	Colourless	Slate to violet	Colourless
Clayton yellow (cotton)	Brownish	...	Orange	Colourless	Red orange	Colourless
Cotton yellow G (cotton)	Brick-red	Red	Greener	...	Crimson	Colourless
Chrysophenin (cotton)	Red violet	Violet	Little change	...	Violet	Colourless
Mimosa (cotton)	Dull dark yellow	...	Orange	...	Orange	...
Cureumin S (extra) (cotton)	Reddish-brown	...	Lighter	...	Duller	...

Orange Colours—*Continued.*

HNO_3 Sp. Gr. 1.42.	$\text{SnCl}_2 + \text{HCl}$.	10% Sol. NaHO .		NH_4HO Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Dirty red spot, dark violet rim	...	Darker	...	Slightly darker	Light pink	Light yellow
Dull yellow spot	Little or no change	Redder	...	Redder	...	Little or no action
Dirty yellow spot	...	Redder	...	Redder	...	Little or no action
...	Decolorised	Darker	...	Lighter	...	Light yellow
...	Decolorised	Lighter	...	Lighter	...	Greenish-yellow
Violet to brown	Decolorised	Orange (reddish)	...	Orange	...	Yellow
Dull crimson	Decolorised	Blue-scarlet	...	Blue-scarlet	...	Little action
Dull crimson	Decolorised	Blue-scarlet	...	Orange	...	No change
Brown	Light orange	No change	...	No change	...	Light yellow
Yellow	Little change	Orange	...	No change	...	Light yellow
Dark red	Slowly yellow	Dark crimson	...	Darker	...	Light yellow
...	Decolorised	Pink	...	Orange	...	Light yellow
Lighter	Light orange	Deep scarlet	Colourless	Orange	Colourless	Little action
Crimson	Decolorised	Red-orange	Pink	Slightly redder	Colourless	Little action
Decolorised	Orange	Scarlet	Colourless	Orange	Colourless	Light yellow
Crimson	Decolorised	Red-orange	Orange	Little change	...	Light yellow
Violet	Decolorised	No change	...	No change	...	Light yellow
...	Nearly decolorised	Orange-red	...	Orange	...	Yellow
...	Decolorised	Redder	...	Redder	...	No change

COLOURING MATTER.	Concen. H_2SO_4 .		10% Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Cresotin yellow G (cotton)	Red-violet	Violet	Lemon	Colourless	Red-violet	Colourless
Diamine yellow N paste (cotton)	Red-violet	Violet	Lighter	Colourless	Red-violet	...
Benzo orange R (cotton)	Blue	Blue	Greenish-blue	Colourless	Blue	Colourless
Toluylene orange R (cotton)	Brown	Brown	Red	...	Dark red	...
Mikado orange 4 R (cotton)	Bright blue	...	Yellower	...	Light olive	...
Mikado orange R (cotton)	Greyish-blue.	...	Yellower	...	Light olive	...
Congo orange (cotton)	Deep blue	Blue	Brown	...	Violet	...

RED

Barwood (chrome mord.)	Terra-cotta	...	No change	...	Redder	...
Camwood (chrome mord.)	Dark crimson	Red	No change	...	Dark crimson	Colourless
Sanderswood (chrome mord.)	Brown	Brown	No change	...	Browner	...
Brazilwood (chrome mord.)	Greenish-brown	Yellow	Little change	...	Dark crimson	...
Brazilwood (alum mord.)	Reddish-brown	Brown	Crimson on standing	...	Red	Pink
Cudbear	Dirty brown	...	Brighter	...	Lighter	Red
Madder (chrome mord.)	Little or no change	Red	Orange	...	Brown	...
Cochineal (tin mord.)	Dark purple	Crimson	Darker	...	Lighter	Red
Lac dye (tin mord.)	Dark purple	Purple	Darker	...	Little or no change	...

Orange Colours—*Continued.*

HNO_3 Sp. Gr. 1.42.	$\text{Sn Cl}_2 + \text{HCl}$	10% Sol. Na HO .		$\text{NH}_4 \text{HO}$ Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Violet	Decolorised	Red	Pink	Orange	Colourless	Yellow
Violet	Decolorised	Red-orange	Faint pink	Orange	Colourless	Yellow
Brown	Decolorised	Crimson	Colourless	Scarlet	Colourless	Light orange
...	Redder	Redder	Colourless	No change	...	Light orange
Dark slate	Decolorised	No change	...	No change	...	Little action
Green olive	Decolorised	Little change	...	No change	...	Little action
Crimson	Decolorised	No change	...	No change	...	Light orange

COLOURS.

Greenish-yellow spot	Brighter	Brown	Brown	Brown	Colourless	No action
Brown spot	Brighter, solution pink	Dark purple	Red	Dark purple	Colourless	No action
Greenish-brown spot	Brighter, solution pink	Dark brown	Brown	Dark brown	Colourless	No action
Yellow spot, red rim	On boiling bright crimson, solution crimson	Maroon	Violet	Violet	Violet	Yellow
Yellow spot, red rim	On boiling scarlet, solution red	Dark crimson	Crimson	Maroon	Violet	Yellow
Yellow spot, red rim	Decolorised	Violet	Violet	Violet	Violet	Bluish-red
Yellow spot	Terra-cotta	Purple	...	Crimson	...	No action
Yellow spot	Darker, solution orange-red	Crimson	Deep crimson	Crimson	Pink	No action
Brown spot	No change	Dark violet	Purple	Dark violet	Colourless	No action

Red Colours—

COLOURING MATTER.	Concen. H ₂ SO ₄ .		10% Sol. H ₂ SO ₄ .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Methyleosin (Berlin)	Orange-yellow	Bright yellow	Slowly decolorised	...	Light yellow	..
Eosine J L (Bindschedler)	Bright orange; changing to brownish-yellow	Canary-yellow	Bright reddish-yellow	...	Bright red-dish-yellow	...
Azo-eosin (By.)	Purple	Purple	Crimson	Pink
Rose bengale (B.A.S.F.)	Reddish-brown	...	Slowly decolorised	...	Decolorised	...
Rose bengale B (Bindschedler)	Bright scarlet, changing to orange and then dirty yellow	Reddish-yellow	Slowly decolorised	...	Decolorised	...
Phloxin (M.L.B.)	Bright orange, changing to brownish-yellow	...	Slowly decolorised	...	Dull yellow	...
Phloxin 2 B (Bindschedler.)	Reddish-brown	...	Decolorised	...	Salmon-red	...
Magenta	Brownish-yellow	Yellow	Darker and bluer	Colourless	Yellow	Faint yellow
New magenta (M.L.B.)	Yellow	Yellow	Darkmaroon, changing to brown	Colourless	Yellow	Faint yellow
Acid magenta (M.L.B.)	Brown-yellow	Colourless, pink on dilution	Little change	...	Much lighter	Pink
Safranine R S (Cas.)	Dark green	Light green	Bluer	Colourless	Dark blue	Faint yellow
Scarlet R (M.L.B.)	...	Pink	Brighter	...	Duller	Pink
Scarlet 2 R (M.L.B.)	Crimson	Crimson	Little change	...	Slightly darker	Pink
Scarlet 3 R (M.L.B.)	Bluer	Bluish-scarlet	No change	...	Little change	Pink
Brilliant double scarlet 3 R (By.)	Dark violet	Red-violet	Brighter	...	Red-violet	...
Brilliant scarlet R (Cas.)	Crimson	Crimson	Little change	...	Darker	Pink
Brilliant scarlet 4 R (Cas.)	Purple	Purple	Little change	...

Continued.

HNO ₃ Sp. Gr. 1.42.	Sn Cl ₂ + H Cl.	10% Sol. Na H O.		NH ₄ H O Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Bright yellow spot	Decolorised	Darker	Pink	Brighter	Pink	Pink (fluorescent)
Yellow spot	Orange-yellow	Brighter	Pink	Brighter	Pink	Bluish-pink on boiling
...	Decolorised	Orange	...	Orange	Orange	...
Yellow spot	Decolorised	Slightly darker	...	No change	Pink	Pink
Yellow spot	Decolorised	Darker	...	Darker	Pink	Bluish-pink on boiling
...	Decolorised	Little change	Pink	Little change	Pink	Pink with greenish fluorescence
Greenish-yellow spot	Decolorised	Darker	...	Darker	Pink	...
Yellow spot	Slowly decolorised	Nearly decolorised	...	Slowly decolorised	...	Deep bluish-red
Bright yellow spot	Slowly decolorised	Nearly decolorised	...	Slowly decolorised	...	Deep bluish-red
Yellow spot	Little or no change	Decolorised	...	Decolorised	...	Pink on boiling
Red-blue spot	...	No change	...	No change	...	Red with fluorescence, on heating
Yellow spot, orange rim	Very slowly decolorised	Yellower	...	Brighter	...	Little action
Dirty yellow spot, light crimson rim	Very slowly decolorised	Orange-red	...	Brighter	Pink	...
Yellow spot	Very slowly decolorised	Red-orange	Light red	Little change	Colourless	Little action
Yellow spot, red-violet rim	Decolorised	Slightly darker	...	Pink
Yellow spot	Slowly decolorised	Brown	...	Little change	Pink	...
...	...	Brown	Light brown	Slightly darker	Pink	...

COLOURING MATTER.	Concen. H_2SO_4 .		10% Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Crystal scarlet (Cas.)	Deep violet	Deep violet	No change	...	Crimson	...
Scarlet 6 R (M.L.B.)	Violet	Blue-violet	No change	...	Crimson	Pink
Scarlet G G (M.L.B.)	Much darker	Scarlet	No change	Pink
Scarlet S (extra) (Berlin)	Bluer	Blue	No change	...	Brown	Faint blue
Fast red A (B.A.S.F.)	Deep bluish-violet	Violet	No change	...	Dull purple	...
Fast red B (B.A.S.F.)	Violet	Bluish-red	No change	...	Dull crimson	Pink
Fast red C (B.A.S.F.)	Reddish-violet	Violet	No change	...	Darker	Pink
Fast red D (B.A.S.F.)	Violet	Violet	No change	...	Darker	Pink
Fast red E (B.A.S.F.)	Dark purple	Purple	Brighter	...	Red-maroon	Pink
Fast red B T (By.)	Violet	Violet	Darker	...
Milling red R (Cas.)	Deep reddish-blue	Reddish-blue	Slightly darker	...	Brownish-maroon	...
Bordeaux (extra) (By.)	Violet	Violet	Dark violet	...
Bordeaux G (By.)	Bright deep blue; red on diluting	Dark blue; red on diluting	No change	...	Blue-violet	Light blue
Orchil red (B.A.S.F.)	Dark blue	Blue	Violet	...
Scarlet 2 S (Berlin)	Reddish-orange	Pink	Yellower	Pink
Crocein scarlet 3 B (By.)	Dark blue	Deep blue	Dark blue	Light blue
Crocein 3 B X (By.)	Purple	Purple	Crimson	Pink
Brilliant crocein (Cas.)	Violet	Violet	Dark red-blue	Light blue
Crocein scarlet 7 B (By.)	Dark blue	Blue	Slightly darker	...	Dark blue	Light blue
Palatin scarlet (B.A.S.F.)	Crimson	Magenta	Darker	Pink

Continued.

HNO ₃ Sp. Gr. 1.42.	SnCl ₂ + HCl.	10% Sol. NaHO.		NH ₄ HO Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Yellow spot, crimson rim	...	Brown	Pink	Light pink on boiling
Yellow spot	...	Brown	Pink	...
...	...	Orange-red	Pink	...
Yellow spot, brown rim	Crimson	Violet	...	Bluer	Bluish-pink	...
Yellow spot, dark red rim	Lighter	Maroon	...	Darker	...	Pink on boiling
...	Lighter	Brownish- red
Yellow spot	Lighter	Brighter	Pink	Pink on boiling
...	Lighter	Dirty brown	...	Darker	Brownish	...
Yellow spot, dull scarlet rim	Brighter	Dark red- brown	...	Darker	Red	Pink
Yellow spot, pur- ple rim	Lighter	Brick-red	...	Darker	...	Red on boiling
Orange-red spot	...	Redder	...	Little change
Yellow spot, blue rim	Bluer	Darkmaroon	Reddish- brown	Crimson	Pink	Light pink on boiling
...	...	Dark purple	...	Slightly darker	...	Pink
Yellowish-orange spot, blue rim	...	Brownish- maroon	...	Dull crimson	...	Pink on boiling
Yellow spot, orange rim	...	Orange	...	Much yellower
Yellow spot, blue rim	Decolorised	Purple	Pink	...
Yellow spot	Decolorised on boiling	Red-brown	...	Browner
Greenish-blue spot, dark blue rim	Decolorised	Purple	...	Bluer
Dark blue spot	Brown	Brownish- purple	...	Brighter	Pink	...
Yellow spot, orange rim	...	Red-brown	...	Lighter

COLOURING MATTER.	Concen. H_2SO_4 .		10% Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Palatin red (B.A.S.F.)	Deep blue	Blue	Little change	...	Bluer	...
Roxamin (Durand)	Bluish-violet	Violet	Little change	...	Bluer	...
Azo-Carmin (B.A.S.F.)	Dark green	Bright green	No change	...	Darker	Red
Cochineal red A (B.A.S.F.)	Crimson	...	No change	...	Darker	...
Cochineal red 3 R (B.A.S.F.)	Purple	Purple	No change	...	Purple	Purple
Erythrosin (extra)	Orange-red ; changing to yellow- brown	...	Orange- yellow	...	Orange- yellow	...
Cyanosin (spirit soluble) (M.L.B.)	Bright orange ; changing to brown- yellow	...	Redder	...	Orange-red	...
Safrosin (Levinstein)	Dirty greenish- yellow	Yellow	Slowly decolorised	...	Nearly decolorised	...
Rhodamine B (B.A.S.F.)	Decolorised ; restored on dilution	...	Brighter	...	Decolorised ; restored on dilution	...
Violamin B or Fast Violet B (M.L.B.)	Bright scarlet	Dull red	Blue-violet	...
Violamin R or Fast Violet R (M.L.B.)	Red	Dirty red	Bluer	Pink
Cyclamin (Monnet)	Reddish- brown	Brown	Decolorised	...	Flesh colour	...
Azo-fuchsin G (By.)	Bluish- violet	Violet-black	No change	...	Brighter	Pink
Azo-fuchsin B (By.)	Dull crimson	Dirty red	No change	...	Little or no change	Pink
Fluoresceïn (B.A.S.F.)	Dirty yellow	Yellow	Lighter	...	Bright yellow	Yellow
Oreil substitute V (Poirrier)	Crimson	Crimson	Darker	...	Crimson	Light crimson
Oreil substitute 3 V N (Poirrier)	Crimson	Crimson	Darker	...	Crimson	Light crimson

Continued.

H N O ₃ Sp. Gr. 1.42.	Sn Cl ₂ + H Cl.	10% Sol. Na H O.		N H ₄ H O Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
...	Nearly decolorised	Brown	Light brown	Redder
Yellow spot, blue rim	...	Brownish-purple	...	Purple	...	Light red on boiling
...	...	Maroon	...	Bluer	Pink	Crimson on boiling
Yellow spot, brown rim	...	Brown	Brown	...	Pink	...
Yellow spot, red-blue rim	Lighter	Dark-brown	Light brown	...	Pink	...
...	Orange-yellow	Little or no change	...	Little change	Pink	...
Yellow spot, orange rim	Bright orange-red	Little or no change	...	Little change	...	Pink, with yellowish-green fluorescence on boiling
Yellow spot	Decolorised	Darker; changing to orange-red	...	Darker	Pink	Pink on boiling
Yellow spot	Brighter	Bluer	Colourless	Slightly bluer	Colourless	Pink (fluorescent)
Bright scarlet spot	...	Red-violet	...	Redder	Pink	Light violet in cold
Dull scarlet spot	Bluer	Cherry-red	Pink	...
Yellow spot	Decolorised	Pink	...
Yellowish-orange spot	Decolorised rapidly	Reddish-violet	Dirty violet	Bright scarlet	Red	Faint red on boiling
Dull red spot	Slowly decolorised	Cherry-red	...	Orange-red	Orange	Faint red on boiling
...	Light yellow	...	Yellow; strong green fluorescence	...	Yellow-green fluorescence	Strong green fluorescence
Yellow spot	Lighter	Maroon	...	Light maroon
Yellow spot	Lighter	Darkmaroon	...	Maroon	...	Pink

COLOURING MATTER.	Concen. H_2SO_4 .		10% Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Orehil red G (Berlin)	Dark purple	Light purple	No change	...	Crimson	Pink
Orseillin (By.)	Dark blue	Blue	No change	...	Violet	...
Cloth red G (Oehler)	Violet	Deep blue	No change	...	Dark red-violet	Light blue
Cloth red B (By.)	Dark navy-blue	Blue-black	No change	...	Dark violet	...
Cloth red 3 G (extra) (By.)	Dark navy-blue	Blue-black	No change	...	Dark violet	...
Clayton cloth red (Clayton)	Purple; on diluting red	Violet; on diluting red	Brighter	...	Dull crimson	...
Purpurin (chrome mord.) (B.A.S.F.)	Bright crimson	Crimson	Slightly bluer	...	Maroon	Red
Alizarin G G (on chrome) (B.A.S.F.)	Dark crimson	Dull crimson	Yellower	...	Dark brown	Slightly yellow
Alizarin V (on chrome) (B.A.S.F.)	Dark crimson	Dirty crimson	Yellower	...	Dark red-brown	Faint yellow
Alizarin bordeaux B (chrome) (By.)	Deep red-violet	Deep violet	Maroon	Dirty brown
Alizarin red S (powder) (chrome) (B.A.S.F.)	Brown	Brownish-red	Yellower	...	Light brown	...
Alizarin maroon (chrome) (B.A.S.F.)	Dark cherry-red	Deep red	Darker	...	Darker	Dirty brown
Congo red (cotton)	Deep blue	Blue	Indigo-blue	Colourless	Blue	Colourless
Brilliant congo R (cotton)	Deep bright blue	Blue	Duller	Colourless	Olive-brown	Colourless
Delta purpurin (cotton)	Deep bright blue	Blue	Reddish-brown	Colourless	Light olive	Colourless
Congo red 4 R (cotton)	Deep bright blue	Blue	Dull purple	Colourless	Deep blue	Colourless
Benzo purpurin B (cotton)	Deep greenish-blue	Blue	Dull red	Colourless	Olive	Colourless
Benzo purpurin 4 B (cotton)	Deep blue	Blue	Dark slate	Colourless	Bright blue	Colourless
Benzo purpurin 10 B (cotton)	Indigo-blue	Blue	Blue	Colourless	Blue	Colourless

Continued.

HNO_3 Sp. Gr. 1.42.	$\text{Sn Cl}_2 + \text{H Cl}$	10% Sol. Na HO .		$\text{NH}_4 \text{HO}$ Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Yellow spot, light crimson rim	...	Slightly darker	...	Brighter	Light red	Faint red on boiling
Dirty yellow spot, blue rim	Slowly decolorised	Reddish-violet	Faint violet	Red-violet	Faint violet	Faint red on boiling
Dirty red spot, dark violet rim	...	Much darker	...	Slightly darker	...	Deep scarlet in cold
Yellow spot, dark purple rim	Slightly bluer	Crimson	...	Crimson	Pink	Crimson
Yellow spot, dark purple rim	...	Darker	...	Brighter	..	Light red
...	Slightly darker	Crimson	...	Brighter and slightly darker	Pink	Light red
Yellow spot, dull orange rim	Brighter	Dark purple	Pink	Darker	...	Little action
Orange-yellow spot	Darker	Darkmaroon	...	Maroon	Colourless	Little action
Orange-yellow spot	Brown	Darker	...	Darker	Colourless	Little action
Dull red spot	...	Bluish-violet	Blue	Bluish-violet	...	Little action
Bright yellow spot	Terra-cotta	Purple	Violet	Purple	Colourless	No action
Brownish-yellow spot, brown rim	...	Darker	...	Darker	...	Little action
Blue	Blue at first; finally decolorised	No change	...	No change	...	Light red
Light red	Slowly decolorised	Slightly yellower	...	No change	...	Light red
Yellow	Decolorised	No change	...	No change	...	Light red
Orange	Blue; finally decolorised	Little change	...	Little change	Pink	Light orange
Light brown	Decolorised	Yellower	...	Little change	Pink	Light red
Yellow	Decolorised	Little change	...	Little change	Pink	Light red
Yellow	Decolorised	Little change	...	Little change	..	Light red

COLOURING MATTER.	Concen. H_2SO_4 .		10% Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Rosazurin (cotton)	Deep greenish-blue	Greenish-blue	Little change	...	Olive	Colourless
Diamine fast red (cotton)	Deep reddish-blue	Blue	Duller	Colourless	Red-violet	Colourless
Erika B (cotton)	Purple	Violet	Redder	Colourless	Redder	Colourless
Diamine scarlet B (cotton)	Bluish-violet	Violet	Little change	...	Violet	Violet
Hessian purple N (cotton)	Greenish-blue	Greenish-blue	Dull violet	Colourless	Blue-violet	Colourless
Brilliant purpurin R (cotton)	Deep blue	Blue	Dull violet	...	Dull blue	Colourless
Hessian brilliant purple (cotton)	Light blue	Light blue	Little change	...	Grey	Colourless
Diamine red N O (cotton)	Deep blue	Blue	Dull violet	Colourless	Olive	Colourless
Diamine red 3 B (cotton)	Deep greenish-blue	Blue	Browner	Colourless	Yellow	Colourless
Delta purpurin 5 B (cotton)	Deep bright blue	Blue	Dull purple	...	Brown	...
St. Denis red (cotton)	Dark crimson	Crimson	Little change	...	Bluer	Colourless
Geranin (cotton)	Crimson	Pink	Little change	...	Little change	...
Naphthylene red (cotton)	Dull blue	Blue	Dull violet	Colourless	Bluish-green	Colourless
Congo corinth G (cotton)	Deep blue	Blue	Blue	Colourless	Blue	Colourless
Congo corinth B (cotton)	Deep blue	Blue	Violet	Colourless	Reddish-blue	Colourless
Magenta (cotton)	Yellow	Yellow	Olive	Yellow	Yellow	Yellow
Safranine (cotton)	Green	Light green; violet on dilution	Little change	Light pink	Blue	Blue
Crocein scarlet 3 B (cotton)	Reddish-blue	Blue	Little change	Pink	Deep blue	Blue

Continued.

H N O ₃ Sp. Gr. 1.42.	Sn Cl ₂ + HCl.	10 % Sol. Na H O.		N H ₄ H O Sp. Gr. '830.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Light brown	Decolorised	Little change	...	No change	...	Faint red
Brown	Dull purple; finally decolorised	Brown	Colourless	Little change	...	Light pink
Light red	Very slowly decolorised	Slightly bluer	Colourless	Little change	Pink	Faint pink
Crimson	Decolorised	Orange	Colourless	Orange	...	Pink
Brown	Decolorised	Little change	Colourless	A little redder	Pink	Bluish-red
Yellow	Decolorised	No change	...	No change	Faint pink	Faint pink
Yellow	Decolorised	No change	...	No change	...	No action
Light brown	Decolorised	Little change	...	Little change	Pink	Light red
Light brown	Decolorised	Little change	...	Little change	Pink	Orange-red
Decolorised	Decolorised	Brighter	...	Brighter	Light red	Red
Little change	Decolorised	Orange	Light orange	Orange	Orange	Red
Little change	Decolorised	Violet	Colourless	Violet	Violet	Faint pink
Olive-green	Decolorised	Little change	...	Little change	...	Faint pink
Brown	Decolorised	Redder	Colourless	Brighter	Pink	Light red
Brown	Decolorised	Much redder	Colourless	Much redder	Pink	Bluish-red
Yellow	Yellow	Nearly decolorised	...	Decolorised	...	Deep bluish-red
Green	Decolorised	Duller	Pink	Little change	Pink	Crimson
Blue at first, then green, and finally yellow.	Decolorised	Nearly decolorised	Grey	Lighter	Scarlet	Scarlet

BROWN

COLOURING MATTER.	Concen. H_2SO_4 .		10% Sol. H_2SO_4 .		HCl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Naphthylamine brown (B.A.S.F.)	Bright blue	Blue	No change	...	Darker	Blue
Fast brown (By.)	Reddish-violet	Reddish-violet	No change	...	Dull maroon	Pink
Fast brown (M. L. B.)	Bluer	Blue	No change	...	Dark crimson	Pink
Fast brown 3 B (Berlin)	Dark blue	Red-blue	Violet	Faint violet
Fast brown G (Berlin)	Dirty brown	Red	Darker	Brown	Chocolate-brown	...
Acid brown R (Berlin)	Dark violet	Violet	No change	...	Dark violet	Violet
Acid brown G (Berlin)	Dirty purple	Purple	Brighter	...	Darker	Faint yellow
Bismarek brown G G	Purple ; restored on dilution	Red-brown	Darker	Colourless	Maroon	Red
Cloth Brown (red shade) (By.)	Very dark violet	Violet	Much darker	Colourless	Dark violet	...
Dioxin (on chrome) (Leonhardt)	Dark green	Green	Little change	...	Darker	Light brown
Gambin (on chrome) (Read Holliday)	Dark brown	Light brown	Redder	...	Little change	...
Anthracene brown	Redder	Brown	No change	...	Yellower	Light brown
Benzo brown 5 R (cotton)	Crimson	Crimson	Little change	...	Little change	Pink
Diamine brown V (cotton)	Dark reddish-blue	Reddish-blue	No change	...	Little change	...
Congo brown R (cotton)	Violet	...	Yellower	Colourless	Blue-violet	...
Cotton brown R (cotton)	Crimson	Crimson	Little change	...	Little change	Light orange
Toluylene brown (cotton)	Dark violet	Violet	Greener	Colourless	Darker	Pink
Congo brown V (cotton)	Blue-violet	Violet	Lighter	...	Violet	Colourless
Congo brown N B R (cotton)	Dark blue	Dull blue	Bluer	...	Red-violet	Colourless

COLOURS.

HNO_3 Sp. Gr. 1.42.	$\text{SnCl}_2 + \text{HCl}$	10% Sol. NaHO .		NH_4HO Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Dirty yellow spot, maroon rim	Little change	Bluish- crimson	Colourless	Crimson	Crimson	...
Yellow spot, maroon rim	Lighter	Dull scarlet	...	Yellower	Yellow- brown	...
Yellow spot, scar- let rim	...	Darker	...	Darker	...	Light red
Yellow spot, orange rim	Bluer	Crimson	...	Crimson	Pink	...
Yellow spot, maroon rim	Lighter	Yellow
Greenish-yellow spot, purple rim	Nearly decolorised	Bright scarlet	...	Scarlet	Pink	Light yellow on boiling
Dirty yellow spot, light maroon rim	Little change	Slightly darker	...	Brighter	Faint brown	Brown on boiling
...	Lighter	Browner	...	Little change	...	Yellow on boiling
Dull red spot, dark violet rim	Little change	Darker	...	Darker
...	...	Very dark green	...	Dark green	Faint red	...
Brownish-yellow	Redder	Yellower	Light yellow	Little change	...	Little action
Dull orange spot	Little change	Olive to black	Colourless	Olive to black	Colourless	No action
Yellow-brown	Yellow	Little change	...	No change	...	Light orange
Dull violet	Nearly decolorised	Little change	Pink	Little change	...	Light red
...	Decolorised	Crimson	...	Lighter	...	Faint brown
Brown	Lighter	No change	...	No change	...	Yellowish-orange
Brown	Decolorised	Little change	...	No change	...	No action
Dark red	Decolorised	Crimson	Pink	Scarlet	Pink	Light brown
Little change	Lighter	Redder	Colourless	Redder	Pink	Brown

Brown Colours—

COLOURING MATTER.	Concen. H_2SO_4 .		10% Sol. H_2SO_4 .		H Cl Sp. Gr. 1.16.	
	Fibre.	Solution.	Fibre.	Solution.	Fibre.	Solution.
Cotton brown A (cotton)	Dark green	...	Little change	...	Darker	Colourless
Cotton brown N (cotton)	Bluish-black	Grey	Darker	Colourless	Darker	Light brown
Benzo brown B (cotton)	Dark purple	...	Darker	...	Darker	Light brown
Benzo brown G (cotton)	Darker	Grey	No change	...	Dark brown	Light brown
Mikado brown G (cotton)	Violet	Violet	Yellower	...	Buff	Colourless
Hessian Brown 2 B (cotton)	Dirty blue-violet	...	Duller	...	Drab	...
Congo brown G (cotton)	Dark violet	Violet	Little change	...	Violet	Colourless

Continued.

HNO ₃ Sp. Gr. 1.42.	SnCl ₂ + HCl.	10% Sol. NaHO.		NH ₄ HO Sp. Gr. .880.		Alcohol.
		Fibre.	Solution.	Fibre.	Solution.	Solution.
Little change	Decolorised	No change	...	No change	...	Brown
Darker	Lighter	Little change	...	Little change	Light orange	Brown
Darker	Lighter	Little change	...	Little change	Faint brown	Light brown
Darker	Lighter	Little change	...	Little change	Faint orange	Light brown
Olive	Decolorised	Little change	...	No change	...	Little action
...	Decolorised	Little change	...	Little change	...	Light brown
Dark violet	Decolorised	Crimson	Crimson	Redder	...	Yellow

APPENDIX.

Systems of Weights and Measures.

Weights.—The English standard unit of weight is 1 *pound* avoirdupois containing 7000 grains.*

- One pound (lb.) = 16 ounces.
- 1 ounce (oz.) = 16 drachms.
- 1 quarter = 28 lbs.
- 1 hundredweight (cwt.) = 4 quarters.
- 1 ton = 20 cwt.

In the metrical system, the gramme (the weight of 1 cubic centimetre of water at 4° C.) is taken as unit for small weights, and the kilogramme (the weight of 1000 cubic centimetres, or 1 litre of water at 4° C.) for greater quantities.

The gramme is divided into 10 decigrammes, 100 centigrammes, or 1000 milligrammes.

- 1 gramme = 15.4323 grains.
- 1 kilogramme = 2.204597 lbs., or
- 10 kilogrammes = 22 lbs., approximately.

One gallon of water weighs approximately 10 lbs.

The weight of 1 cubic foot of water is 62.424 lbs. (= 1000 ozs. nearly).

Measures.—The English standard unit of length is 1 *yard*, which is subdivided into 3 feet, 36 inches, or 432 lines.

The units used as the measures of surfaces and volumes are the square and cube respectively of the linear units.

- Thus—
 - 1 square yard = 9 square feet.
 - 1 square foot = 144 square inches.
- And
 - 1 cubic yard = 27 cubic feet.
 - 1 cubic foot = 1728 cubic inches.

The legal measure of capacity is, however, the *Imperial gallon*—that is, a volume holding 70,000 grains or 10 lbs. (avoirdupois) of distilled water at the temperature of 62° F., and under a barometric pressure of 30 inches. The Imperial gallon contains, therefore, 277.274 cubic inches.

- 1 gallon = 4 quarts.
- 1 quart = 2 pints.
- 1 pint = 4 gills.

The standard unit of length in the metrical system is the *metre*, which is somewhat longer than the yard.

* The English measures of weight, length, and capacity, are also used in the United States, with the exceptions, however, that the legal measure of capacity is the apothecary's or wine gallon, and that a short ton = 2,000 lbs. is very generally employed, the English ton = 20 cwt. being called a gross ton. 1 wine gallon = 231 cubic inches = 3.785 litres.

- 1 metre = 10 decimetres = 100 centimetres = 1000 millimetres.
 1000 metres = 1 kilometre.
 1 metre = 1.093633 yards = 3.2809 feet = 39.3708 inches.
 64 metres = 70 yards, approximately.

The measure of capacity is the *litre*—that is, a volume equal to that of 1 cubic decimetre or 1000 cubic centimetres.

For small volumes the *cubic centimetre* (generally written cc.) is taken as unit.

- 1 litre = 0.220097 gallon = 61.027 cub. in.
 = $1\frac{3}{4}$ pints, approximately.
 1 hectolitre (100 litres) = 22 gallons, approximately.

Specific Gravities.

By *specific gravity* or *density* is meant the weight of a solid or liquid compared with the weight of an equal volume of water at 4° C. By the metrical system, the weight of one cubic centimetre of the substance in grammes gives at once its specific gravity.

The specific gravity of solid bodies may be determined by weighing a piece of the substance, first in the air, and then in distilled water; the difference in weight will indicate the weight of water displaced, and the specific gravity can be thus calculated. Or, the weight of water displaced by a known weight of the substance is determined in the specific gravity bottle.

Of much greater importance to the dyer is the determination of the specific gravity of liquids or solutions, for the purpose of determining their degree of purity or of obtaining a rough estimate of the amount of substance dissolved. The most exact results are arrived at by means of the specific gravity bottle—a small glass bottle or flask, generally of 25 or 50 cc. capacity, provided with a stopper, through which a fine hole is pierced. The flask is filled with the liquid or solution under examination, the stopper inserted, and the superfluous liquid which escapes through the hole in its centre is wiped off. The flask containing the solution is now weighed, a counterweight exactly equal to that of the empty flask being placed on the opposite pan of the balance. If the flask is one of 25 cc. capacity, the weight in grammes thus obtained will give at once the weight of 25 cc. of the solution, and dividing this by 25, will give the specific gravity. If, for instance, the weight of the liquid were found to be equal to 30 grammes, the specific gravity of the liquid would be $\frac{30}{25} = 1.20$. In case no other apparatus is at hand, a determination may be made by measuring 10 cc. of the liquid from a pipette, and weighing it in a tared flask. In order now to ascertain the amount of substance in solution, it is necessary to refer to tables which have been constructed for most of the substances used in dyeing, with the exception of the dyes themselves. Thus, if the solution under examination had been one of sulphuric acid, and showed a density of 1.11, we should refer to the table on p. 148, and see at a glance that the solution contained 16 per cent. of sulphuric acid (H_2SO_4). Or, if it were one of stannic chloride, we should refer to the table for stannic chloride on p. 286, and see that it contained 18 per cent. of stannic chloride ($\text{SnCl}_4 + 5\text{H}_2\text{O}$), and so on.

It should be borne in mind that in estimating the strength of solutions by determining their specific gravities, the results will be of no value whatever if more than one substance be in solution. Thus the specific gravity of a solution of nitrate of iron, containing an admixture of Glaubersalt, is valueless, since it does not tell us to what extent the increase in the density of the liquid is due to the nitrate of iron or the sodium sulphate.

In determining specific gravities, it should also be remembered that temperature materially affects the correctness of the results. Most of the tables are constructed for 15° C. or 60° F., and the determinations should consequently be done as nearly

as possible at this temperature. The following may serve as an instructive example of the effect of temperature on the density:—If a small quantity of aniline-oil is poured into a test-tube containing pure water, it will sink at the ordinary temperature, the oil being then slightly heavier than water. But the coefficient of expansion of aniline-oil is greater than that of water, and, on heating the contents of the tube, the oil slowly rises, and ultimately floats on the surface, having now a less specific gravity than water.

Hydrometers.—The specific gravity bottle is not often employed in dye-houses, its place being taken in the works by the more convenient hydrometers. The hydrometer most in use consists of a glass tube (the stem), with a large and a small bulb at the end. The large bulb is filled with air to give the instrument buoyancy, while the smaller bulb at the bottom serves for the reception of shot or mercury, which causes it to stand vertically in a liquid. For liquids heavier than water, the size of the larger bulb and the quantity of mercury are so regulated as to cause the stem to sink within about half an inch of the top in distilled water at 60° F. This point is marked 1·000. By immersing the instruments in liquids of known specific gravity, and noting each time the point to which the stem rises out of the liquid, the other values are obtained, which are transferred to a scale inside the stem. For liquids lighter than water, the point marked 1·000 is made to show at the bottom of the stem; the graduation is done as before.

In the specific gravity hydrometer, the differences corresponding to equal increases in density are not equal, so that an accurate graduation of the tube shows unequal intervals.

By means of such hydrometers the specific gravity of a liquid can be determined by simply immersing the instrument in the liquid contained in a glass cylinder, and reading off the specific gravity at the point to which the stem sinks into the liquid. Care should, of course, be taken that the instrument does not touch the side of the vessel.

Hydrometers graduated in degrees, such as those of Twaddle, Baumé, Beck, Cartier, are in much more general use than the specific gravity hydrometer.

The degrees in *Twaddle's* hydrometer, which is in general use in England, bear a direct relationship to the specific gravity. The degree Twaddle is obtained from the specific gravity by the following rule: Multiply by 1000, subtract 1000, and divide by 5. Thus, in order to convert the specific gravity 1·205 into degrees Twaddle, we have—

$$\begin{array}{r} 1\cdot205 \times 1000 = 1205 \\ \quad \quad \quad 1000 \\ \hline 5 \overline{) 205} \\ \quad \quad 41^{\circ} \text{ Tw.} \end{array}$$

To convert degrees Twaddle into specific gravity: Multiply by 5, add 1000, and divide by 1000. Thus for 32° Tw. we should have the following:—

$$\begin{array}{r} 32 \times 5 = 160 \\ \quad \quad \quad 1000 \\ \hline 1000 \overline{) 1160} \\ \quad \quad \quad 1\cdot160 \text{ spec. gravity.} \end{array}$$

On the Continent and in the United States, Baumé's hydrometer is in general use. The degrees in the Baumé hydrometer mostly used on the Continent are calculated (according to Lunge and Hurter, *Alkali-maker's Handbook*, p. 175) by the formula $d = \frac{144\cdot3}{144\cdot3 - n}$, water of 15° C. being put = 0° B and sulphuric acid of 1·842 at 15° C. = 66° B. In the above formula, d indicates the specific gravity and n the number of degrees Baumé.

In another Baumé hydrometer the scale is graduated by assuming as normal points for liquids heavier than water—

0° in pure water.

15° in 17 parts of water and 3 parts of common salt.

For liquids lighter than water, the normal points assumed are—

0° in 9 parts of water and 1 part of common salt.

10° in pure water.

The size of a single degree is thus easily obtained in either case, and the graduating is done with these degrees.

For liquids lighter than water the specific gravity values, and not degrees, are used in England.

COMPARATIVE TABLE OF HYDROMETER DEGREES BAUMÉ
AND TWADDLE.

B.	Tw.	B.	Tw.	B.	Tw.	B.	Tw.
1	1.4	18	28.4	35	64.0	52	112.6
2	2.8	19	30.4	36	66.4	53	116.0
3	4.4	20	32.4	37	69.0	54	119.4
4	5.8	21	34.2	38	71.4	55	123.0
5	7.4	22	36.0	39	74.0	56	127.0
6	9.0	23	38.0	40	76.6	57	130.4
7	10.2	24	40.0	41	79.4	58	134.4
8	12.0	25	42.0	42	82.0	59	138.2
9	13.4	26	44.0	43	84.8	60	142.0
10	15.0	27	46.2	44	87.6	61	146.4
11	16.6	28	48.2	45	90.6	62	150.6
12	18.2	29	50.4	46	93.6	63	155.0
13	20.0	30	52.6	47	96.6	64	159.0
14	21.6	31	54.8	48	99.6	65	154.0
15	23.2	32	57.0	49	103.0	66	168.4
16	25.0	33	59.4	50	106.0	67	173.9
17	26.8	34	61.6	51	109.2	68	...

Thermometers and Thermometric Scales.

Thermometers serve for indicating the degree of temperature, and they are useful, if not indispensable, to the dyer in carrying out many operations of washing, mordanting, dyeing, ageing, and drying. The thermometer most in use is the ordinary mercurial thermometer. Three scales are in use—namely, those of Fahrenheit, Réaumur, and Celsius (the Centigrade scale). Of these the Fahrenheit scale is used principally in this country and in the United States, the Réaumur scale in Germany and Austria, while the Celsius or Centigrade scale, used in France and Scandinavia, although used principally for scientific purposes, is gradually taking the place of the two older scales.

In the graduating of a thermometer, two points are taken as standards—viz., the freezing point and the boiling point of water at a pressure equal to that of 760 mm. of mercury. For the different scales these are fixed at the following points:—

		Freezing Point.	Boiling Point.
Fahrenheit,	. . .	32°	212°
Réaumur,	. . .	0°	80°
Centigrade,	. . .	0°	100°

Therefore, 180° F. = 80° R. = 100° C.

To convert the degrees in one scale into those of another we have the simple formulæ:—

C. to R.	$^{\circ}\text{R.} = \frac{9}{5}^{\circ}\text{C.}$
R. to C.	$^{\circ}\text{C.} = \frac{5}{9}^{\circ}\text{R.}$
C. to F.	$^{\circ}\text{F.} = \frac{9}{5}^{\circ}\text{C.} + 32.$
F. to C.	$^{\circ}\text{C.} = \frac{5}{9} (^{\circ}\text{F.} - 32).$
R. to F.	$^{\circ}\text{F.} = \frac{9}{4}^{\circ}\text{R.} + 32.$
F. to R.	$^{\circ}\text{R.} = \frac{4}{9} (^{\circ}\text{F.} - 32).$

TABLE FOR CONVERTING DEGREES CENTIGRADE (CELSIUS) INTO DEGREES FAHRENHEIT.

Fahr.	Cels.	Fahr.	Cels.	Fahr.	Cels.
32	0.00	102	38.88	172	77.77
34	1.11	104	40.00	174	78.88
36	2.22	106	41.11	176	80.00
38	3.33	108	42.22	178	81.11
40	4.44	110	43.33	180	82.22
42	5.55	112	44.44	182	83.33
44	6.66	114	45.55	184	84.44
46	7.77	116	46.66	186	85.55
48	8.88	118	47.77	188	86.66
50	10.00	120	48.88	190	87.77
52	11.11	122	50.00	192	88.88
54	12.22	124	51.11	194	90.00
56	13.33	126	52.22	196	91.11
58	14.44	128	53.33	198	92.22
60	15.55	130	54.44	200	93.33
62	16.66	132	55.55	202	94.44
64	17.77	134	56.66	204	95.55
66	18.88	136	57.77	206	96.66
68	20.00	138	58.88	208	97.77
70	21.11	140	60.00	210	98.88
72	22.22	142	61.11	212	100.00
74	23.33	144	62.22	214	101.11
76	24.44	146	63.33	216	102.22
78	25.55	148	64.44	218	103.33
80	26.66	150	65.55	220	104.44
82	27.77	152	66.66	222	105.55
84	28.88	154	67.77	224	106.66
86	30.00	156	68.88	226	107.77
88	31.11	158	70.00	228	108.88
90	32.22	160	71.11	230	110.00
92	33.33	162	72.22	232	111.11
94	34.44	164	73.33	234	112.22
96	35.55	166	74.44	236	113.33
98	36.66	168	75.55	238	114.44
100	37.77	170	76.66	240	115.55

Evaporation and Boiling.

Evaporating.—When water is exposed to the air it evaporates—that is, its particles pass into the surrounding atmosphere in the form of vapour. The rate of evaporation will depend upon the amount of moisture present in the air, the barometric pressure, the velocity of the air, and the temperature. In a perfectly dry atmosphere, or in a vacuum, the following figures show the effect of temperature in this respect:—

TABLE SHOWING THE BAROMETRIC PRESSURE OF SATURATED
AQUEOUS VAPOUR IN MILLIMETRES FOR A
GIVEN TEMPERATURE.

Degrees C.	Millimetres.	Degrees C.	Millimetres.
- 10	2·09	50	91·98
0	4·6	55	117·48
+ 5	6·53	60	148·79
10	9·16	65	186·94
15	12·70	70	233·08
20	17·60	75	288·50
25	23·55	80	354·62
30	31·55	85	433·00
35	41·83	90	525·40
40	54·91	95	633·69
45	71·39	100	760·00

In a perfectly dry current of air the rate of evaporation in drying, for instance, would be proportional to these figures.

Boiling.—As will be seen from the foregoing table, the tension of aqueous vapour becomes at 100° C. equal to that of the pressure of the atmosphere. Water is then said to boil—that is, if it is exposed to the air at the ordinary barometric pressure. But if confined in closed vessels (a boiler, for instance) the following relations between pressure and temperature are observed :—

Degrees C.	Pressure.	Degrees C.	Pressure.
100	1 atmosphere.	159·22	6 atmospheres.
120·60	2 „	165·34	7 „
133·91	3 „	170·81	8 „
144·00	4 „	175·77	9 „
152·22	5 „	180·31	10 „

Dissolved substances materially affect the boiling point of water. Thus, a saturated salt solution only boils at 109° C. Soluble salts are sometimes added to the dye-bath for the purpose of raising the boiling point of water.

The boiling point of water is also affected by the pressure of the atmosphere. The greater the height above sea-level at which the works are situated, the lower will be the boiling point of the water. Ordinarily, the difference is very small, and has no material influence; but under certain conditions it might materially affect certain dyeing operations. By exhausting the air from a vessel containing water, the liquid may be made to boil at the ordinary temperature.

In transforming water into vapour or steam, a large amount of energy (in the form of heat) has to be overcome. In physics the amount of heat is measured by heat units or *calories*, one calorie being the amount of heat necessary to raise a unit (1 gramme) of water through 1° C. Thus, in order to raise 1 gramme of water from 0° to 100° C., 100 calories would be required. The same amount of heat would suffice on the other hand to raise 100 grammes of water from 0° to 1°, or from 5° to 6°, or 25 grammes of water from 0° to 4°, and so on. But in order to raise 1 gramme of water at 100° into steam of the same temperature, the amount of heat required is no less than 537 calories. In the operations of drying, or in the use of open dye-vessels or non-condensing engines, the quantity of so-called *latent heat* which thus passes away into the surrounding atmosphere is absolutely lost for all practical purposes. In like manner a great loss of heat may be sustained by condensation in steam-pipes which are badly or insufficiently insulated.

The heat apparently lost in the conversion of water into steam shows itself again in the condensation of the steam into water, 1 gramme of steam at 100° containing sufficient heat to raise 537 grammes of water 1° C. Thus, in the heating of

dye-vats by steam practically no heat need be lost if the pipes are well insulated, the steam merely serving as a convenient medium for transferring the heat produced in the boiler to the part of the works in which it is required.

With a properly constructed furnace, 1 lb. of coal should convert not less than 7 lbs. of water into steam at 100° , and this might be practically taken as equivalent to $7 \times 537 = 3759$ pounds-calories. From this it would, for example, be easy to calculate the amount of coal necessary to raise a 300 gallon vat of water from the ordinary temperature (say 10° in winter) to boiling point. Using the pound as unit in the calorie, we have 300 gallons or 3000 pounds to be raised from 10° to 100° , or through 90° C. = 3000×90 , or 270,000 pound-calories.

Now 3759 pound-calories require 1 lb. coal.

Or 1 " " $\frac{1}{3759}$ "

And 270,000 pound-calories require $270,000 \times \frac{1}{3759} = 72$ lbs. about.

And taking the coal at 10s. per ton, this would represent about 4d. in coal.

A calculation of this kind can only give a rough estimate, no account being taken of possible condensation in the pipes, but it is practically independent of the pressure in the boiler.

HygroscoPy.

Moisture in the Air.—When water evaporates it is taken up or dissolved by the surrounding atmosphere. The amount of water capable of being thus absorbed varies directly with the pressure and temperature of the air. When the evaporation has proceeded for a certain time in a closed space the air becomes incapable of absorbing any further quantities of water, and is then said to be saturated.

In the operation of "ageing," it is frequently necessary to ascertain the relative moisture in the chamber. This is generally effected by means of the wet- and dry-bulb thermometers, the latter being an ordinary thermometer, while the bulb of the former is kept moist by being enveloped in wet muslin or calico. The drier the air the more rapidly will the water round the wet-bulb thermometer evaporate. In evaporating, the water absorbs heat from its immediate surroundings, and the temperature consequently falls in proportion to the dryness of the air. In an atmosphere saturated with moisture, the two thermometers will show the same degree of temperature. The amount of moisture actually present in the air can be obtained by reference to tables. This, however, is seldom done in the works, the difference in the temperatures of the two thermometers being a sufficient guide to work by.

Another instrument for measuring the moisture in the atmosphere is the hair-hygrometer, the action of which depends upon the fact that a hair will expand in a moist atmosphere, and contract in a dry one. Of the various instruments constructed on this principle, that of Saussure, as improved by Hottinger (see Fig. 116), deserves attention.

It contains a well-cleansed hair, made fast at its upper end, while the lower end passes round a small pulley, to which is attached a finger. The hair is kept stretched by means of a weight of half a gramme attached to its lower extremity. When drying, the hair contracts, and draws the finger to the left; when moistened, it expands, and the weight draws the finger to the right. The instrument is enclosed in a small glass case when not in use. Before being used it is tested by simply inserting a sliding frame of wetted muslin into the case. The air will quickly become saturated with moisture, and the corresponding temperature is read off in the thermometer. The index of the hygrometer should now rise to 100; if this is not the case it is brought to that point by turning the index or

finger. After withdrawing the wet muslin, the hygrometer is exposed to the atmosphere, the moisture of which is to be determined. The point on the scale at which the index remains stationary indicates directly the percentage of saturation of the air by moisture.

When air saturated with moisture is cooled, the moisture condenses and becomes visible as fog or mist. This is especially the case on a cold day in dye-houses where many open dye-vats are being used. Under such conditions the whole room is frequently filled with such a dense fog that the work may become impeded. The admission of cold air from the outside only makes matters worse, causing more condensation. By heating the air before it enters the room, the fog or "steam" could be done away with to a great extent or altogether. The evil is also greatly lessened by fixing a wooden hood, connected with a flue, directly over each dye-vat, so that the steam is drawn off before it has time to get into the air of the room.

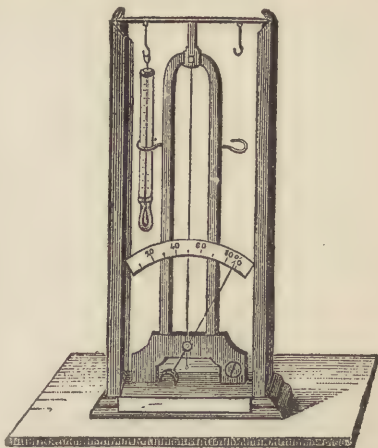


Fig. 116.—Hottinger's hair-hygrometer.

Light and Colour.

According to the present accepted theory, light is produced by the rapid undulatory or wave movements of the universal ether. These movements take place in any direction perpendicular to the path of the ray in ordinary light, whereas in so-called polarised light the ether oscillates in one plane only. The wave-lengths as well as the number of oscillations per second vary with different kinds of light, as is seen from the following measurements of Fresnel:—

COLOUR OF LIGHT.	Wave-lengths in air, expressed in millimetres.	Number of oscillations per second (in billions).
Violet, . . .	0·000423	735
Dark-blue, . . .	0·000449	691
Light-blue, . . .	0·000475	653
Green, . . .	0·000511	607
Yellow, . . .	0·000551	563
Orange, . . .	0·000583	532
Red, . . .	0·000645	500

When a ray of light passes from one transparent medium into another of different density, its path is altered, and the light is said to be *refracted*. The degree of refraction varies with the difference in the density of the two media and with the wave-length, those rays being refracted most which have the smallest wave-length. Thus, by passing a ray of white light through a glass prism, we are able to decompose it into its constituent parts; in other words, to analyse it. White sunlight decomposed in this manner yields a so-called *spectrum*, in which the eye is able to detect the following colours—red, orange, yellow, green, blue, and violet. The coloured light in 1000 parts of white sunlight is distributed, according to Rood, as follows:—

Red,	54	Yellowish-green,	121
Orange-red,	140	Green and blue-green,	134
Orange,	80	Sky-blue,	32
Orange-yellow,	114	Blue,	40
Yellow,	54	Ultramarine and blue-violet,	20
Greenish-yellow,	206	Violet,	5

The solar spectrum contains besides, other rays beyond the violet (ultra-violet rays) and beyond the red (ultra-red or heat rays), which are not visible to the eye.

Each colour in the spectrum consists of uniform or homogeneous light; it cannot be further decomposed. But the colours which we perceive in everyday life never consist of homogeneous light; they are always mixtures of differently coloured rays. This fact can be readily demonstrated by means of the *absorption-spectrum*, produced by passing a ray of white light through a solution of the colour, and observing the result in the spectroscopic, or by the direct analysis of the light reflected from the object in the same instrument. Thus, a solution of picric acid in water, and a piece of flannel dyed with this colouring matter, both produce in our eye the impression of an intense yellow. But when we come to analyse the yellow in the manner indicated, we shall find that it not only contains the yellow of the spectrum, but also all the rays from the red end as far as the blue and violet, which latter are extinguished. The light entering our eye contains indeed all the yellow of the spectrum, but in addition to this it contains the red, green, and bluish-green parts of the spectrum. But these are balanced in such proportions as to produce white, and our impression of yellow is caused, therefore, by the pure yellow of the spectrum mixed with a large proportion of white light. Similarly, a solution of magenta does not appear red because it allows only the red rays of the spectrum to pass, but because it absorbs that portion of the spectrum which is *complementary* to it—viz., the green—allowing all the rest to pass, and our impression of red is, therefore, produced by the red of the spectrum mixed with a large proportion of white. Again, a solution of indigo extract gives an absorption-spectrum which shows a dark band in the yellow. It allows the blue and all the other rays to pass, except yellow, with the result that a blue mixed with a large proportion of white is produced. Other colouring matters behave in a similar manner; no colour is known which allows only homogeneous light to pass. To the presence of white light in a colour is due in a great measure its brilliancy.* Each dyestuff has its own characteristic absorption-spectrum, and on this will depend to a very great extent its behaviour in admixture with other colours and its appearance under different illuminations. To the absorption-spectra are also due the effects produced by mixing two or more colouring matters. Thus picric acid and indigo extract yield green, but the effect of green is not produced by the one only allowing yellow rays, the other only blue rays to pass, but because both allow the green rays to pass through unchanged, accompanied by a certain amount of white light.

It has already been seen that white solar light can be decomposed into a number of coloured lights. By reuniting these, white light is again produced. The same effect, viz., white, is also produced by mixing two lights, the colours of which are complementary to each other,—for instance, orange and indigo, red and green. Exactly the opposite is the case with *solutions* of two complementary colours. Thus a solution of two such complementary colours as indigo-blue and orange, if sufficiently concentrated, allows no light to pass through, and a black results. If the solution be diluted far enough greys will result—i.e., mixtures of black and white.

The behaviour of dyed textile fibres is analogous to that of the solutions of the

* See A. Scheurer, "On yellow and the limit of the yellow sensation," *Journ. Soc. Dyers and Col.*, p. 195, 1891.

corresponding dyestuffs. The fibres are all translucent, and hold the colours or rather their lakes in a state of solid solution. The light which strikes a piece of dyed material penetrates to a certain distance into the substance of the fibre, is deprived of some of its constituents, and is reflected back, entering the eye with the same result as would have been obtained by passing it through a solution of the dyestuff or dyestuffs employed.

The three simple or *primary* colours at present adopted by physicists are red, green, and blue. But for several reasons it is better for the dyer to accept as his primary colours the older classification of red, yellow, and blue. Add to these black and white, and we have all the primary impressions which the eye is capable of receiving. From red and yellow we obtain orange, from yellow and blue, green, and from blue and red, violet. Red, yellow, and blue mixed together in the right proportion give black or grey, as is the case with the complementary colours.

The colour of an object will depend to a very great extent on the nature of the light with which it is illuminated. This is a matter of fact which few can have failed to observe in everyday life. Even during the day-time there is a marked contrast between the green colour of the leaves of trees and of meadows in the morning and evening, which is not due to a change in the green, but to a change in the light. Still more marked is the contrast shown by many colours in bright day-light and in gas- or lamp-light. Most yellow, green, blue, and certain compound shades are very difficult to judge by gas-light. Some colours appear totally different by gas- or lamp-light to what they do by day-light. One of the most striking examples of this kind is the green produced by a mixture of acid violet 7 B and naphthol-yellow S. By day-light it is a full, but not very brilliant, green, whereas by gas- or lamp-light it is not possible to detect in it the slightest trace of green; it is simply a dull violet. In the dyeing of compound shades, due notice should be taken of this and similar facts. One can easily imagine, for instance, the result in a yarn-dyed figured dress-fabric, if two lots of the yarn had been dyed the same colour but with different dyestuffs by different dyers, and used by the manufacturer indiscriminately either in the warp or weft. The pieces would look all right in the day-time, but at night the effect might be grotesque. But could not this fault be turned to practical account in the manufacture of dress-goods which would appear plain in day-light, and in figured designs of different colours at night, or *vice-versa*? The range of colouring matters applicable for such a new departure in dyeing is certainly not very great at present, but it is not by any means improbable that it may be considerably increased in the near future.

The best light for the matching of colours during the day-time is that coming from the north, because it is least subject to variations. A north top-light is, therefore, generally chosen by dyers for matching off. When day-light is not available, the most convenient substitute for it is the electric arc-light. Incandescent lamps are not much better than gas and cannot compare with the arc-light. Although the latter is not in every sense a perfect substitute for sun-light, it renders valuable services during the short winter days and in foggy weather, and has consequently been introduced in a large number of dyeworks.

If an arc-light is not available, the next best substitute for day-light is magnesium wire or ribbon. The thick wire is best, because it burns more steadily and more slowly than the thin wire or the ribbon. It does not take fire readily in an ordinary gas flame, but can be easily lighted in a Bunsen. Where neither the arc-light nor magnesium wire are available, Swedish safety matches are sometimes employed. The first flash produced on striking the match and lasting about one second is pretty rich in blue and violet rays.

For fuller details on the subject of Light and Colour, the reader may refer to the following works:—Chevreul on *Colour*; Rood's *Modern Chromatics*; Church's *Colour* (Cassell & Co.).

TABLE OF THE ELEMENTS, THEIR SYMBOLS AND ATOMIC WEIGHTS.

HYDROGEN, H = 1.

NAME.	Symbol.	Atomic Weight.	NAME.	Symbol.	Atomic Weight.
1. Aluminium, .	Al	27·1	36. Nickel, . .	Ni	59(?)
2. Antimony } (Stibium), }	Sb	120	37. Niobium, . .	Nb	94·2
3. Arsenic, . .	As	75	38. Nitrogen, . .	N	14
4. Barium, . .	Ba	137	39. Osmium, . .	Os	192
5. Beryllium, .	Be	9·1	40. Oxygen, . .	O	16
6. Bismuth, . .	Bi	208	41. Palladium, .	Pd	106
7. Boron, . . .	B	11	42. Phosphorus,	P	31
8. Bromine, . .	Br	80	43. Platinum, .	Pt	194·8
9. Cadmium, . .	Cd	112·1	44. Potassium } (Kalium), }	K	39·1
10. Caesium, . .	Cs	132·9	45. Rhodium, . .	Rh	103
11. Calcium, . .	Ca	40	46. Rubidium, .	Rb	85·4
12. Carbon, . .	C	12	47. Ruthenium, .	Ru	103·8
13. Cerium, . .	Ce	140·2	48. Samarium, .	Sa	150(?)
14. Chlorine, . .	Cl	35·5	49. Scandium, .	Sc	44·1
15. Chromium, .	Cr	52·3	50. Selenium, . .	Se	79·1
16. Cobalt, . .	Co	59(?)	51. Silicon, . .	Si	28·4
17. Copper, . .	Cu	63·3	52. Silver (Ar- gentum), }	Ag	108
18. Didymium, .	Di	147(?)	53. Sodium } (Natrium), }	Na	23
19. Erbium, . .	Er	166(?)	54. Strontium, .	Sr	87·5
20. Fluorine, . .	F or Fl	19	55. Sulphur, . .	S	32
21. Gallium, . .	G or Ga	69·9	56. Tantalum, .	Ta	129
22. Germanium, .	Ge	72·3	57. Tellurium, .	Te	125
23. Gold (Aurum),	Au	197·2	58. Thallium, . .	Tl	204·1
24. Hydrogen, .	H	1	59. Thorium, . .	Th	232·4
25. Indium, . .	In	113·7	60. Thulium, . .	Tu	171(?)
26. Iodine, . . .	I	126·9	61. Tin (Stannum),	Sn	118·1
27. Iridium, . .	Ir	193·2	62. Titanium, . .	Ti	48·1
28. Iron (Ferrum),	Fe	56	63. Tungsten } (Wolfram), }	W	184
29. Lanthanum, .	La	138·5	64. Uranium, . .	U	239·4
30. Lead (Plum- bum), . . }	Pb	206·9	65. Vanadium, . .	V	51·2
31. Lithium, . .	Li	7	66. Ytterbium, .	Yb	173·2
32. Magnesium, .	Mg	24	67. Yttrium, . .	Y	88·7
33. Manganese, .	Mn	55	68. Zinc, . . .	Zn	65
34. Mercury (Hy- drargyrum), }	Hg	200·4	69. Zirconium, .	Zr	90·7
35. Molybdenum,	Mo	95·9			

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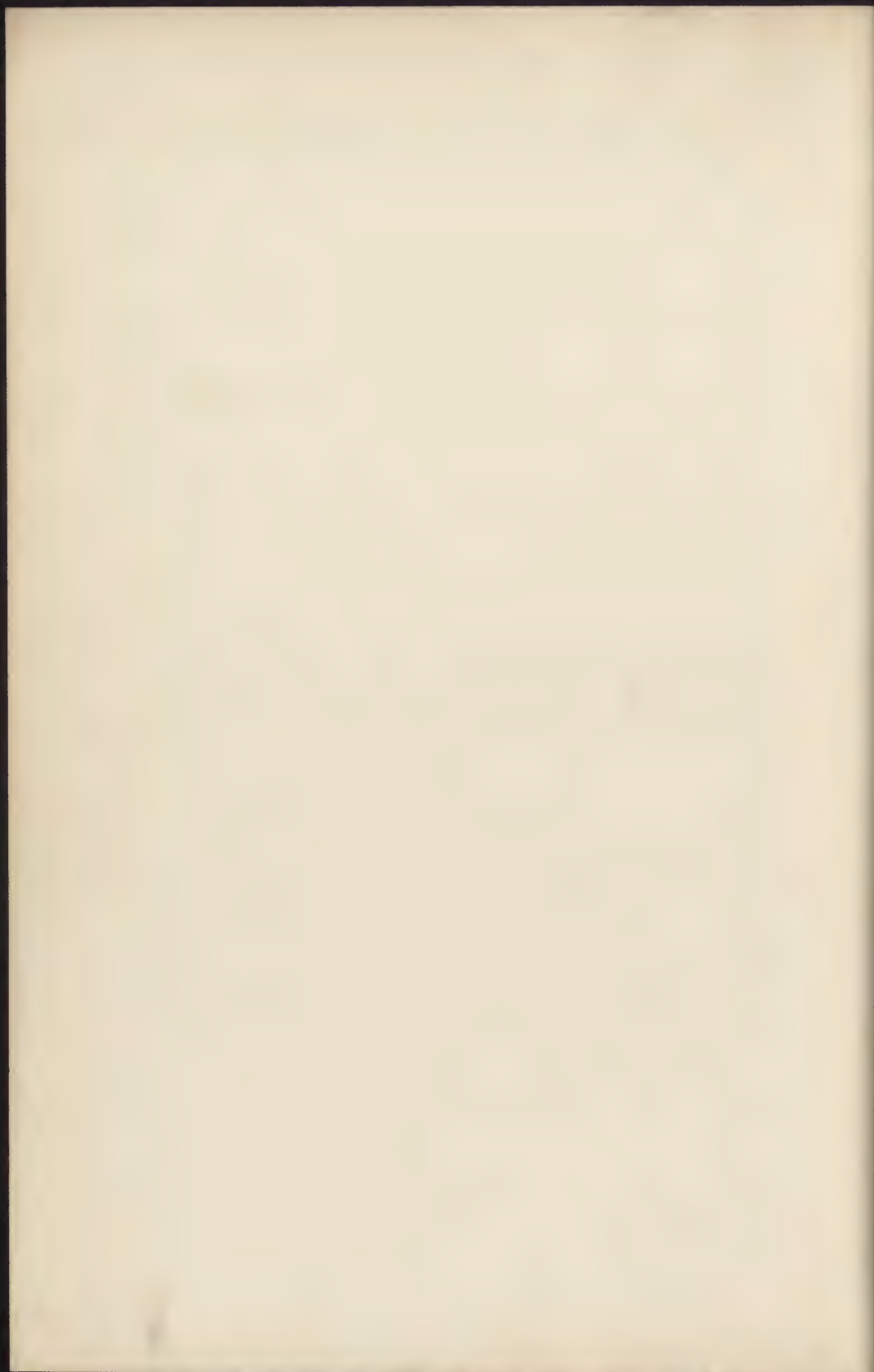
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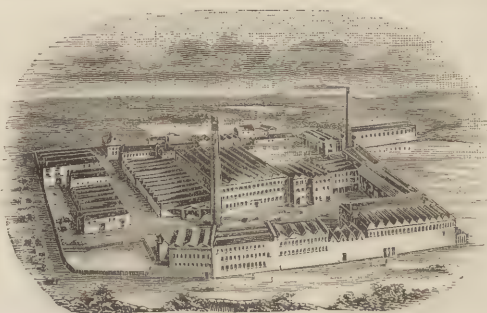
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